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PHYSICAL REVIEW.

LIGHT PRODUCED BY THE RECOMBINATION OF IONS.

By C. D. Child.

CERTAIN phenomena connected with the luminosity of the vapor rising from the mercury arc indicate that this light is produced by the recombination of ions, and that the vibrations of the atoms producing light are not started when the atoms are broken into ions, but when the ions recombine into atoms.[1] Since this conclusion is contrary to that held by some who have investigated the problem of the production of light from a different standpoint, it is desirable to modify in some way the experiment to which reference has been made. In that experiment the current was continuous and the vapor was examined after it had moved away from the region where the current was flowing. The experiment can be modified by stopping the current and examining the vapor in the place where the current has been flowing; that is by examining the light from an alternating current arc at the moment when no current is flowing. If the light is due to recombination it will in either case continue for a time after the current has ceased flowing through the vapor. If the light is due to ionization, it will cease when there is no ionization and this occurs when no current passes through the vapor.

An examination of the light at different phases has already been made by Fleming and Petavel[2] and they found that at the moment when there is no current there is a very appreciable amount of light given off not only by the carbons, but also by the gas between the carbons. They also found that the minimum of light occurs after the time when the current is zero. It occurs, in fact, at approximately the same time as the minimum of conductivity, that is, the time when there is the least number of ions. These experiments were made before the electron

[1] Phil. Mag. (6), 26, 906; 1913, and (6), 31, 139; 1916.

[2] Phil. Mag. (5), 41, 339; 1896.

theory of discharge was developed and no attempt was made by Fleming and Petavel to explain their results. It is evident, however, that the phenomena observed by them are what must occur, if the light is due to recombination. It is also possible to suggest other explanations when carbon electrodes are used in air. For example, the light which appears when there is no current may be due to the oxidation of the hot gases between the electrodes. It, therefore, seemed desirable to repeat their experiments using mercury terminals in a vacuum instead of carbon electrodes in air.

Description of Apparatus.—The apparatus used was essentially the same as that employed by Fleming and Petavel and a more complete description can be found in their article. An outline of the apparatus is given in Fig. 1. *A* is an arc enclosed in a box which shuts off as much

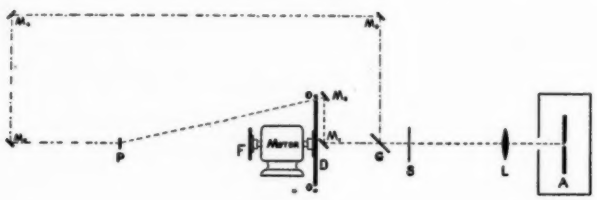

Fig. 1.

of the light as possible. The light from the arc passes through an opening to the lens *L*, which produces the image of the arc on the screen *S*. In this there is an opening which allows the light from the gaseous part of the arc to pass through, but screens off that from the carbons. From this point the light passes to two mirrors, M_1 and M_2, which are fastened upon an arm that can be rotated about the axis of a synchronous motor. *D* is a disk that is rotated by the motor and in this are two openings, *O* and *O*, through which the light passes from M_2 to the Lummer-Brodhun photometer at *P*. Since the motor is in step with the alternations of the arc, this allows the light from some particular phase of the alternation to pass to the photometer and by rotating the arm which carries M_1 and M_2 the light from different phases can be examined.

For a source of comparison an unsilvered glass is placed at *G*. This reflects a small part of the light to M_3 and from there it is reflected to M_4, M_5, and to *P*. In this way the light from the particular phase which is being studied is compared with the total light given off by the gaseous part of the arc, and errors due to changes in the current or due to changes in the position of the arc are eliminated. Since the light coming from M_2 to *P* makes an angle with the photometer bar, the photometer must remain stationary. The mirrors M_4 and M_5 were, therefore, placed on a

movable carrier and the intensity of the light at the photometer was varied by moving this carrier.

In the experiments on the arc in air the distance from A to L was 22 cm.; from L to S, 128 cm.; from S to M_1, 34 cm.; from M_1 to M_2, 17 cm.; from M_2 to P, 125 cm. D was 38 cm. in diameter. The opening O was variable and will be given in connection with the different experiments. The distance from S to the middle of G was 12 cm.; from G to M_3, 50 cm.; and from M_4 to M_5, 50 cm.; while the distances from M_3 to M_4 and from M_5 to P were variable.

There was also attached to the shaft of the motor a contact maker F for obtaining the instantaneous values of the current and potential difference of the arc. The rotating part consisted of a fiber wheel 12 cm. in diameter. At the edge of this a piece of copper 1 mm. wide was embedded. This was connected to a ring collector. The stationary brush which made contact with this was 2 mm. wide and was made of woven copper wire. This brush was placed on an arm which could be rotated about the axis of the motor.

The potential was determined by balancing the potential difference existing between the terminals of the arc at the instant that contact was made against a potential difference which was measured by a Weston voltmeter. The balance was determined by a D'Arsonval galvanometer. The current at any instant was determined by passing it through a known non-inductive resistance and balancing the potential difference between the terminals of the wire against a known potential difference.

The motor used was one made by the General Electric Company. It is wound as an ordinary three-phase induction motor with squirrel cage winding and in starting operates as an induction motor. When up to speed it pulls itself into step and runs as a synchronous motor as long as the load is small. This tendency to run as a synchronous motor is aided by a lack of circular uniformity in the arrangement of the iron of the rotor. When up to speed the rotor behaves much as a four-pole permanent magnet would. This has the disadvantage that it does not always drop into step at the same point. At times it drops into step at one point of the phase and at other times at a point 90 degrees from this. In other respects the motor behaved admirably. There was little trouble from hunting. There was a slight fluctuation in speed, but as far as could be determined this was due to an irregularity in the speed of the generator at the power house. The motor made 1,800 revolutions per min. being on a sixty-cycle circuit. The arc was placed between two of the three wires leading to the motor.

The Carbon Arc.—As a test of the apparatus it was first used to repeat

the observations of Fleming and Petavel on the light from the gaseous part of the arc between carbons. Cored carbons 13 mm. in diameter were used. The arc was 7 mm. long and the current was 12 amperes. The opening at *O* was 20 mm. by 16 mm., the former distance being in the direction of the diameter of the wheel. A stationary screen was placed in front of the mirror *M* having an opening of the same size as that on the rotating wheel. The observations which were made are given in the following table. Column 1 gives the phase angle of the alternating current between an arbitrary starting point and the observed point. Column 2 gives the potential difference in volts corresponding with this position of the brush, column 3 gives the current in amperes and column 4 the relative candle power as computed from the setting of the photometer.

TABLE I.

Phase Angle.	Potential Difference.	Current.	Intensity of Light.	Phase Angle.	Potential Difference.	Current.	Intensity of Light.
0	−17	−2.9		192	0		
10	− 5	.0	.3	200	−15	−2.0	.25
32	0			210	−24	−3.1	.3
20	14	2.0	.3	220	−31	− 6.6	.3
30	24	3.7	.25	230	−35	− 9.5	.7
40	31	6.4	.3	240	−37	−11.2	1.4
50	36	9.2	.8	250	−40	−13.4	2.4
60	39	11.9	1.6	260	−45	−15.0	2.9
70	41	13.6	2.4	270	−54	−16.5	3.2
80	48	15.4	3.1	280	−56	−17.4	3.3
90	55	16.9	3.2	290	−58	−16.9	3.3
100	57	17.2	3.3	300	−56	−15.6	3.2
110	58	16.9	3.3	310	−54	−14.2	3.2
120	57	16.0	3.3	320	−52	−12.5	2.7
130	55	13.9	3.2	330	−48	− 9.9	1.8
140	52	12.5	3.2	340	−38	− 7.9	1.3
150	45	11.0	2.2	350	−30	− 5.7	.7
160	36	8.1	1.3	360	−16	− 3.7	.4
170	25	5.7	.7	370	0	.0	.3
180	15	3.1	.4	380	12	1.5	.3
190		.0	.3				

These curves are plotted in Fig. 2. They are very similar to those shown by Fleming and Petavel (p. 338). Both sets of curves show that the minimum of light occurs after the time of zero current. The time of zero current can be determined with much accuracy, and while it is not possible to determine the time of minimum intensity of light with the same degree of accuracy, there is no doubt but that the time between these two occurrences is approximately 1/20 of a complete cycle, that is, 1/1200 sec. As has already been stated, we can not consider

that this is a proof that the light is due to recombination since the phenomenon is complicated by the possibility that some ionization is caused by the combustion of the hot gases.

The ratio between the candle power when the light is at a minimum and that when it is at a maximum is approximately 1/10. This is the same as that found by Fleming and Petavel. It has been suggested

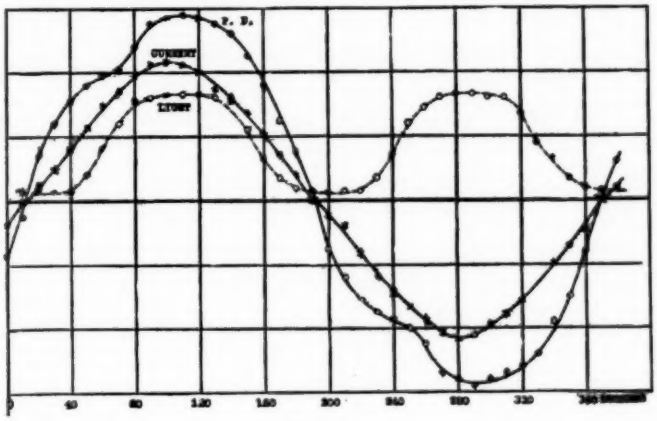

Fig. 2.

that the light which appears to exist at the time of the minimum is due either to stray light or to the fact that the opening at *O* has a very appreciable width. Both of these explanations will be discussed in connection with the flaming arc, where the amount of light at the time of the minimum is much larger than with the carbon arc.

The Flaming Arc.—A study of the flaming arc can give us no proof of the way in which light is produced, since the light at the time of no current may here also be due to oxidation of the hot gases, but, as far as the writer is aware, no data regarding the relation between the current phase of the flaming arc and the intensity of the light has been published. It, therefore, seemed desirable to make such an investigation. The carbons used in this investigation were No. 301, made by Siemens and Halske. These were 8 mm. in diameter. The arc was 9 mm. long and the current was 12 amperes. The opening at *O* was 16.5 mm. in width.

It is difficult to make correct settings of the photometer because of the changes in the color of the light. When the light is at a minimum it is much yellower than the average light with which it is compared. During the remainder of the cycle it is bluer than the average. The observations, however, are sufficiently accurate to give a correct idea of the general relation existing between the current and the intensity of the light. These observations are given in Table II.

TABLE II.

Phase Angle.	Potential Difference.	Current.	Intensity of Light.	Phase Angle.	Potential Difference.	Current.	Intensity of Light.
0	−20	−3.3	100	190			73
10			77	192	0	0	
14	0	0		200	−15	− 1.1	45
20	17		50	210	−32	− 1.3	
30	37	1.1		214			29
34			29	220	−48	− 2.6	42
40	48	2.6	38	230	−49	− 6.6	69
50	49	6.1	58	240	−44	− 9.0	83
60	45	9.7	81	250	−42	−12.5	
70	41	12.3		260	−42	−14.7	90
80	41	14.9	89	270	−43	−15.6	
90	42	16.2		280	−42	−17.6	94
100	40	17.6	92	290	−40	−17.6	
110	40	17.6		300	−40	−16.7	98
120	40	16.9	95	310	−38	−15.8	
130	36	15.0		320	−37	−13.4	105
140	35	14.5	100	330	−34	−11.9	
150	32	12.1		340	−31	− 9.7	110
160	30	9.9	104	350	−26	− 6.2	110
170	28	6.6	104	360	−20	− 3.3	100
180	20	2.6	94	370			77

These data are plotted in Fig. 3. As with the arc between cored carbons we find that the minimum of light does not occur at the time of zero current but about 1/1200 sec. after the current is zero.

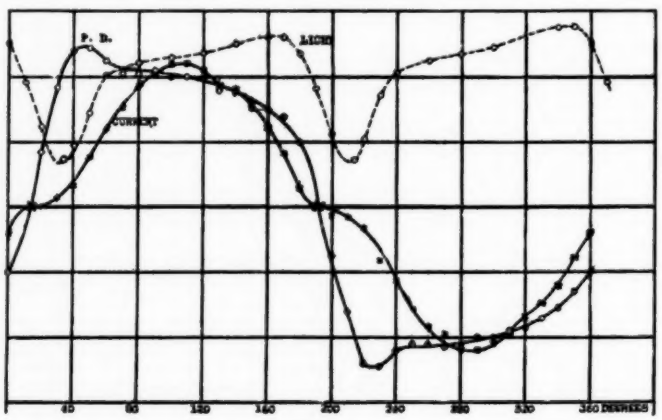

Fig. 3.

Accuracy of Measurement for Minimum Intensity.—In this case the minimum amount of light is approximately ½ of the maximum. No appreciable amount of this is due to stray light, for when the opening either at *O* or at the screen in front of this was closed no light that could be detected passed to the photometer.

There is, however, the possibility that the apparent continuance of light is due to the fact that the opening at *O* has a very appreciable width. It does not give instantaneous values of the light, but values for a finite length of time. For example the width of *O* when the preceding measurements were made was 16.5 mm. The width of the opening in front of this was the same. The center of *O* was 17 cm. from the center of the disk *D*. The time elapsing from the instant when light begins to pass through the opening until it entirely ceases is $\frac{2 \times 16.5}{2\pi \times 170}$ or .031 of the time of one complete revolution of the disk. Since there are two cycles for each revolution of the disk, this would be .062 of a cycle. This may be sufficient to give an apparent value different from the real value.

In order to test this the candle power at the time of minimum was examined with different openings at *O*. If the light passing through the opening were to remain the same during the time that one opening passed the other, the amount of light would vary as the product of the widths of the two openings. If the light is a minimum at the instant the two overlapped, the intensity of the light will decrease when the opening is made smaller more rapidly than the width of the opening. To test this observations of the candle power at the point of minimum intensity of light were made with different sizes of openings in the revolving disk at *O*. These are given in Table III. Column 1 gives the size of opening in the revolving disk. Column 2 gives numbers proportional to the intensity of the light passing this opening as nearly as could be determined by taking the average of several settings. Column 3 gives the ratios between the numbers in the two preceding columns.

TABLE III.

Size of Opening in Disk.	Intensity of Light.	Ratios.
2.24	5.60	2.50
1.58	3.48	2.54
.68	1.75	2.58

The intensity of the light decreases but slightly more rapidly than the width of the opening. This indicates that the real minimum is not more than a few per cent. below that given in Table II.

Spectrum at Different Phases.—As has been stated the color of the light at the time of minimum intensity is yellower than that shown at the time of maximum intensity. On examining the spectrum of the light at different phases it was found that the only spectrum shown with the apparatus used was the calcium spectrum and that the one shown at the

time of minimum intensity was that which is known as the flame spectrum, while at the time of maximum intensity the arc spectrum was shown. This phenomenon has already been investigated by Crew and Spence[1] and by Puccianti[2] and no further knowledge concerning it has been gained by this investigation. It is evident that this fact is quite in harmony with the assumption that the luminosity at the time of no current is due to the oxidation of the hot gases and that it proves nothing concerning the mechanism by which light is produced.

The Mercury Arc.—As is well known it is very difficult to maintain an alternating current arc between mercury terminals. An attempt was made by the writer to do so by using two transformers in series, one giving 4,000 volts and one 2,000 volts. With a slight amount of residual air in the tube this gave a current of several amperes, but with the residual air the sides were soon covered with a film of mercury and became opaque. Without the air it was impossible to maintain an arc. This was true whatever the size of the tubes or the length of the arc, and the attempt to produce the arc in this way was finally abandoned.

An attempt was then made to use an alternating-current arc between a direct-current arc and a third terminal, as shown in Fig. 4. The direct

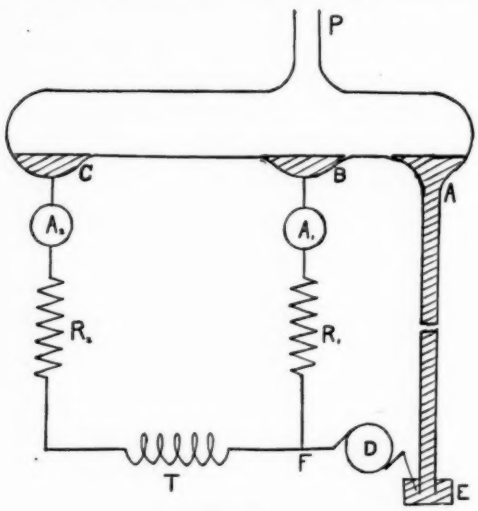

Fig. 4.

current arc was maintained between A and B by means of the dynamo D. A transformer T giving 110 volts was inserted between F and the terminal C. A vertical tube extended from A to the cup E. The arc was started by raising the cup E until the mercury in A made contact with that in B.

[1] Astrophys. Jour., 22, 199; 1905

[2] Physik. Z. S., 8, 470; 1907.

By this means a unidirectional pulsating current was easily maintained between C and A. A cold terminal in the neighborhood of a mercury arc can easily become the positive terminal of a second arc, but can not become the negative terminal. However, there is no objection to this kind of an arc for the work in hand, for all that is needed is a current which passes through zero value at regular intervals.

Different combinations of this arrangement were tried by reversing the polarity of A and B and by changing the position of the resistances, but the arrangement shown in the diagram gave the most uniform and consistent results. The current to B was regulated by means of the resistance R_1 and that to C by means of R_2. The potential difference between A and C was very nearly independent of the current flowing but it is dependent on the amount of vapor in the tube. As the tube becomes heated the density of vapor becomes greater and the potential difference between the terminals becomes greater.

The tube P was connected all the time with the pump, but in spite of this the pressure in the tube varied. Moreover the intensity of the light depends both on the amount of current and on the potential difference. The only way to regulate this is to stop the alternating current arc for a time and to allow the vapor to condense. In making observations the arc was run until the potential difference reached a definite value, the observations were then made and the current stopped for a few minutes allowing the tube to cool. This process was repeated for each observation. By this means data could be obtained at a definite current and potential difference.

The pressure of the vapor was determined by measuring the change in height of the mercury in A. As the pressure increased this column was pushed down and the amount of change was measured by a cathetometer reading to 1/20 mm.

With the mercury arc the light from the terminals can be easily avoided by taking that which comes from the vapor midway between the terminals. The screen S in Fig. 1 was, therefore, omitted and the arc focused on P instead of on S. With this arrangement the distance from A to L was 30 cm. and LM_1 was 22 cm., the other distances remaining approximately the same as before. The inside diameter of the tube was 2.4 cm. The distance from A to B was 9 cm. and from B to C was 18 cm.

The data obtained concerning the mercury arc is given in Table IV., the arrangement being as in the preceding tables. During these readings the current as measured by the ammeter A_2 was 10 amperes and the voltage between C and A was 45 volts. The pressure of the vapor was 1.4 mm.

TABLE IV.

Phase Angle.	Potential Difference.	Current.	Intensity of Light.	Phase Angle.	Potential Difference.	Current.	Intensity of Light.
10	18.4			140			198
20	45.5			150	25.2	17.1	
30	80.5			160			198
40	93.0	1.65		170	25.2	15.3	
50	63.0	4.82	50	180			190
60	33.0	8.3	90	190	24.2	12.6	
70	27.2	11.3	142	200			172
80			160	210	22.3	7.6	
90	25.2	14.6		220	21.3	5.7	114
100			181	230	19.3	3.6	80
110	25.2	17.1		240	17.5	1.8	53
120			194	250	5.8	.43	25
130	25.2	18.0					

Fig. 5 gives the plot for these data. It will be observed that the potential difference and the current continue for more than half of a complete period. This is due to the manner in which the two circuits are connected. When there is no E.M.F. due to the transformer there

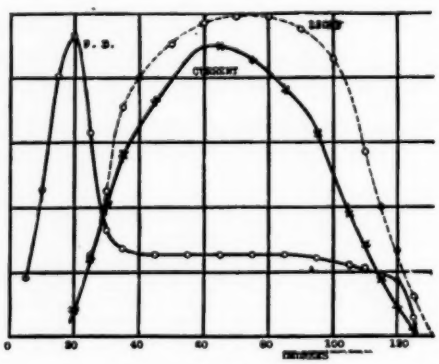

Fig. 5.

is still a potential difference between C and B due to the drop in potential around R_1. From F there is a divided circuit, part of the current flowing through T, R_2, and C to B and part flowing through R_1. The current will continue to flow from F through C until C is approximately at the same potential as B, that is until the E.M.F. of the transformer is equal to the drop in potential through R and in the opposite direction.

The curve for the potential difference shows the usual peculiarities for the alternating current arc in an exaggerated form. The voltage rises to a relatively high value before the current begins to flow. The high voltage is probably required in order to establish the conditions

at the anode essential for the arc form of discharge. A comparatively small number of electrons can pass from a mercury arc to a third terminal without any glow or luminous point on the electrode, but when the discharge becomes larger one or more luminous points are produced by the impact of the negative ions. From these points positive ions move toward the arc, neutralizing the electro-static effect of the negative ions, and the drop in potential near the terminal becomes less. In the case here studied the luminous points must be produced at the beginning of each period. Until they are established the voltage continues to increase and energy is expended in heating the surface of the mercury. When the hot points are once produced less voltage is required and we have a decrease in voltage, as shown in the voltage curve.

Determination of Time of Minimum Intensity.—It is evident from the curves shown in Fig. 5 that the light does not cease at the instant the current ceases, but the exact time when the light vanished could not be determined by means of the photometer. A better arrangement for this purpose is obtained by placing the tube as near to the rotating plate as possible and looking directly at the tube with the rotating plate between the arc and the eye as shown in Fig. 6. As the opening passes the tube one obtains a view of the arc showing the progressive changes during a fraction of a cycle. The width of the opening was decreased to 4 mm., so as to secure as nearly as instantaneous a view as possible.

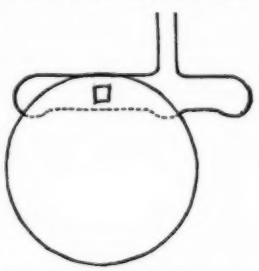

Fig. 6.

With this arrangement it was found that there was a time of minimum intensity occurring shortly after the current ceased, followed by a period of slightly greater luminosity. This gradually died out, being visible, however, during a time equivalent to 34 electrical degrees. The minimum was more pronounced when the pressure of the vapor was small. When the pressure became 1.7 mm. it was no longer possible to detect a point of minimum intensity. A photograph was taken showing this point of minimum luminosity, but it was not found possible to secure one of sufficient value to reproduce. There was a slight irregularity in the speed of the motor of which mention has already been made. This blurred the photograph when a time exposure was taken and with a very short exposure the photograph was too faint to be of value.

This phenomenon seemed to indicate that with the reversal of the E.M.F. a slight current flowed in the direction opposite to that of the main current, that is, flowing from *A* to *C*. A more careful examination with the apparatus previously used for finding the amount of current

showed that such a current existed. When the pressure was low the maximum value of this current was in the neighborhood of .05 ampere. When the pressure increased it became too small to be detected with the apparatus used.

This reverse current is, no doubt, to be explained as follows: Before the ions produced by the flow of current from *B* to *C* have all recombined an electric force is started in the opposite direction. This force is sufficient to cause the electrons to ionize by their impact and a resulting current to flow. The force is not, however, sufficiently high to produce ionization by the impact of positive ions on the cathode *C*. As a consequence no ions are formed to take the place of those which move toward *B*, the field is soon cleared of electrons, and the current ceases.

This action takes place in a small fraction of one cycle, so that we have a momentary current of small magnitude. As the pressure of the vapor increases the mean free path of the electrons becomes less so that there is less chance to ionize the gas. Moreover, the velocity of both the positive and negative ions becomes less. For both of these reasons the reverse current becomes less, as the pressure of the gas becomes greater.

The intensity of the light when at the minimum was much too small to be determined with any apparatus which was at hand. It was, however, quite possible to obtain the time at which the minimum intensity occurred. This was approximately 12 electrical degrees or 1/1800 sec. after the current became zero.

A similar set of readings was taken when the vapor pressure in the tube was 3.23 mm. instead of 1.4 mm. and the current was 8 amperes instead of 10. In this case the potential difference between *A* and *C* as recorded by the A. C. voltmeter was 55 volts instead of 45 volts. The curves found at this pressure were similar to those shown in Fig. 4. The potential difference, however, rose to 104 volts before the current began to flow and was 32 volts when the current was a maximum. The current continued through only 184 degrees instead of 230.

Spectrum at Different Phases.—The light given out at the time of zero current was slightly more yellow than the light of the normal mercury arc. None of the lines of the spectrum disappeared, but the relative intensity changed somewhat. The green line (5,460 microns) and others belonging to the same sub-series being less prominent at the time of zero current. This corresponds to the change observed in the spectrum of the vapor rising from the mercury arc.[1] In both cases the green line is less prominent in the vapor through which no current is passing than it is in the arc itself.

[1] PHYS. REV. (2), 4, 388; 1914.

An attempt was made to study the conduction of the vapor after the main current of the arc had ceased by means of exploring electrodes, but this did not prove successful. In the first place the conductivity of a highly conducting vapor can not be determined with any degree of accuracy by exploring electrodes. In order to remove all of the ions from a region where there are many ions, it is necessary to have a strong field and such a field produces new ions by impact. In the second place, as has been shown, the current does not remain zero for any appreciable length of time, and a knowledge of the conductivity at the time that a current was being started in the opposite direction would not give us any knowledge of the rate at which the ions recombine.

Conclusion.—These results are entirely in harmony with the view that part at least of the light coming from the mercury arc is due to recombination of the ions. The time of maximum intensity occurs after the time of maximum current and the light continues after the current ceases, as is required by such a view. Moreover, if the light is due to recombination, the intensity of light must be greater, the greater the number of ions present. The number of ions present is very approximately proportional to the conductivity of the gas and this in turn is proportional to the current divided by the potential difference, and we find that this relation does in fact exist. Through a large part of the period the voltage is nearly constant and the luminosity changes as the current. At the end of the period both the current and the voltage decrease, but the light is roughly proportional to the ratio between them.

On the other hand these facts are not in harmony with the view that the light is caused by a vibration produced when the atoms are ionized, unless we assume that the atoms continue to vibrate for a comparatively long time after the impact is made which starts the vibration. In the work here described the light continues for at least 1/30 of a cycle after the current ceases, that is for 1/1800 sec. The difficulty of explaining this continuance of the light has already been shown by the author.[1] Strutt[2] also mentions this difficulty, but expresses the belief that it can eventually be explained.

Summary.—The work of Fleming and Petavel on the intensity of the light from an alternating current carbon arc at different phases was repeated and a similar study was made of the flaming arc and mercury arc in a vacuum. In every case the intensity of the light passes through a minimum without entirely vanishing and this minimum occurs after the current passes through the zero value. With the mercury arc the

[1] Phil. Mag. (6), 26, p. 909; 1913.

[2] Proc. Roy. Soc., A, 91, p. 92; 1914.

minimum intensity occurs approximately 1/1800 sec. after the current becomes zero. In this case the continuance of the light indicates that the light is due to the recombination of the positive and negative ions, since there is here no chance for oxidation or other known chemical action.

COLGATE UNIVERSITY,
August, 1916.

COUNTER ELECTROMOTIVE FORCE IN THE ALUMINUM RECTIFIER.

By Albert Lewis Fitch.

I. Introduction.

THE anomalous action of aluminum in the electrolytic cell was first discovered by Wheatstone in 1855. Soon after this, Buff found that an electrolytic cell one electrode of which was aluminum would rectify the alternating current. Among the other men who have been interested in this cell may be mentioned Ducretet,[1] Hutin and Leblanc,[2] Montpellier,[3] Nodon,[4] Guthe,[5] Greene,[6] and Schulze.[7] The latter has perhaps done the largest amount of work of any. His articles have appeared from time to time in a number of magazines.

The earlier experimenters with this cell confined themselves to the study of aluminum but later investigation[7] has shown that many other metals possess this same property to a greater or less degree. Among these may be mentioned iron, nickle, cobalt, magnesium, cadmium, tin, bismuth, zirconium, tantalum, etc.

A great many electrolytes may be used in the rectifier. The most commonly used are the alums, phosphates, and carbonates; however Greatz and Pollak[8] have shown that any electrolyte which will liberate oxygen on electrolysis may be used more or less satisfactorily.

It has been found that the ability of the cell to rectify alternating current depends upon the current density at the aluminum anode,[9] the inductance and resistance of the circuit,[10] and its temperature.[11] The cell works best when the current density is high and the inductance, resistance, and temperature are low.

[1] Comptes Rendus, Vol. 80, p. 280.
[2] French Patents, No. 215945.
[3] Electrician, Vol. 22, p. 17.
[4] Comptes Rendus, Vol. 136, p. 445.
[5] Phys. Rev., Vol. 15, p. 327.
[6] Phys. Rev., Vol. 3, series 2, p. 264.
[7] Zeitschr. Elektrochem., Vol. 14, p. 333.
[8] Elektrotechnische Zeitschr., Vol. 25, p. 359.
[9] Elektrotechn. Zeitschr., Vol. 21, p. 913.
[10] Ann. der Physik, Vol. 39, p. 976.
[11] Zeitschr. Elektrochem., Vol. 14, p. 333.

Two prominent theories have been advanced to explain the action of this cell. The earlier theory, known as *the solid film theory*, ascribes this action to the electrolytic deposition and decomposition of a solid film of some oxide or hydroxide of aluminum on the aluminum anode. The deposition takes place while the current flows in at the aluminum and, being a high resistance material, the film soon grows to a thickness which shuts off the current in that direction. The decomposition takes place when the current is in the opposite direction and permits the current to flow unimpeded from the electrolyte to the electrode.

In 1902 Guthe[1] first gave us the later theory, known as *the gas film theory*. This theory ascribes the action to a film of oxygen gas which is spread over the solid layer. The free electrons of the metal are forced through the gas film by the very high potential gradient with very little difficulty, when the aluminum is the cathode, but when the current reverses, and the aluminum is the anode, no such thing can take place because there are no free electrons in the electrolyte. Instead, the current must be carried through the film by the ions of the electrolyte and these being relatively large as compared to the electrons are with difficulty forced through.

It has been known for a great many years that the aluminum cell acts to a certain extent like a condenser. Schulze[2] states that a cell 40 × 40 × 40 cm. with both plates of aluminum had a capacity of 5,000 mfd. on 160 volts alternating current of a frequency of 50 cycles per second. It was possible, he states, to take an alternating current of 250 amperes through this cell. But one must not go too far in likening this cell to an ordinary leaking condenser as Greene[3] has shown.

This investigation was undertaken to determine if a more careful study of the counter electromotive force, which is produced when current enters at the aluminum, would throw some light on the action of the cell as a condenser and also on the theories advanced.

The cell used was composed of a lead plate with an area of approximately 90 sq. cm. and an aluminum wire .258 cm. in diameter and 10 cm. in length, immersed in a saturated solution of sodium phosphate. The aluminum wire was tested and found to contain .27 per cent. iron and some silicon in the form of silicates. It is about 99 per cent. pure. The lead is the same grade as that used in the chemistry department in qualitative experiments and is believed to be as pure as the aluminum. Both electrodes are heavily coated with a good grade of sealing wax where

[1] PHYS. REV., Vol. 15, p. 327.
[2] Zeitschr. Elektrochem., Vol. 14, p. 333.
[3] PHYS. REV., Vol. 3, series 2, p. 264.

they emerge from the solution to eliminate surface effects which were found to be present when the electrodes were not coated.

II. Experimental Work.

As a preliminary study, a potentiometer method was devised for the measurement of the counter electromotive force. The cell was placed directly across the storage battery terminals for a time with the aluminum as anode and then the counter electromotive force, after a certain period of open circuit, was compared directly with the storage battery voltage. This period of open circuit was adjusted and measured by means of the disk described in the following method. Although this potentiometer method gives very accurate measurements of time of open circuit and of counter electromotive force, it is too slow to give the desired results.

Since the time for taking the readings by the former method could not be decreased, the oscillographic method was devised. This method enables one to take a complete set of readings in about one second. This eliminates to a large degree the objection to the former method and also enables one to get readings for much shorter periods of closed circuit.

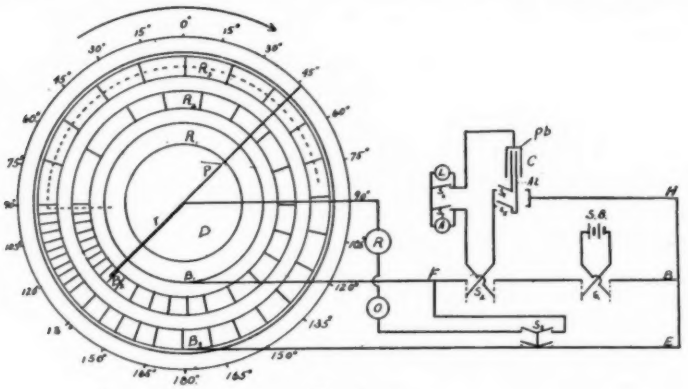

Fig. 1.

The diagram for the arrangement of apparatus is shown in Fig. 1. In this method the same disk was used as before with the same brush contacts and the same electrical connections on the disk. This disk is shown as D. It was designed for this work and made in the engineering shops of the University of Michigan. It is a solid, hard rubber disk of approximately 31 cm. radius. Firmly screwed to this disk are three concentric rings of brass. The inner ring R_1 has an inner radius of 12 cm. and an outer radius of 16 cm. It is made in one solid piece. The second ring R_2 has an inner radius of 19 cm. and an outer radius of 23 cm. It is divided into sectors ranging in magnitude from 5 degrees to

35 degrees. The outer ring R_3 has an inner radius of 26 cm. and an outer radius of 30 cm. It is divided into sectors ranging from 3.75 degrees to 28 degrees. Each sector on each ring is connected electrically to a binding post on the back of the disk. On the circumference of the disk is a steel tire. The disk is mounted on the shaft of a Roth motor, designed to run at 2,000 R.P.M. on 220 volts direct current. This disk is enclosed in a wooden box supported on sliding arms so that the box can be brought as near as desired to the disk and clamped fast. The front of the box holds the brush contacts B_1, B_2, B_3 made of spring steel with brushes of sheet copper. B_1 and B_3 are bolted directly to the box and allow the brushes fastened to them to bear on rings R_1 and R_3. B_2 is a movable brush contact supported on a brass rod bent at right angles and passing through the box front at a point directly in line with the center of the motor shaft. A long brass pointer P is fastened to this brush holder by heavy brass nuts and plays over a protractor of 8 inches radius divided into quarter degrees. On the back of the disk, the sectors are connected as shown by the dotted line. In the back of the box face, a large screw was placed to stop the rotating arm r at the same place each time.

As before, it was arranged to have the cell placed directly across the storage battery when readings were not being taken. S_1 and S_2 make an eight-pole double-throw switch. S_4 and S_5 are double-pole double-throw switches. C is the rectifier. L is a lamp for resistance. A is a Weston ammeter with .01 ampere divisions. L and A may be cut out of the circuit by switches S_6 and S_7. R is a Leeds & Northrup resistance box with a total resistance of 1,111 ohms and O is the vibrator of the Siemens & Halske Oscillograph. The oscillographic chamber was filled with oil to produce the proper damping effect. The cylinder of the oscillograph is connected directly to the motor shaft which rotates the disk. This makes the cylinder and disk rotate in exact synchronism.

The motor is connected with its field over the 220-volt direct current power line and its armature over the storage battery. By this arrangement, any speed up to 2,000 R.P.M. is attainable by varying the number of cells of the storage battery.

ELECTRICAL CONNECTIONS.

It is evident from the figure that there are two paths for the current from the storage battery S.B. to the cell C if S_3 is thrown to the right. It can flow from S.B. to B and H to the cell through either of the switches S_4 or S_5, or it can flow by the path B, E, S_3, F, S_2 to C through either of the switches S_4 or S_5 thrown to the left. This arrangement enables one

to use two anodes of different metals in the same cell and still have them electrically independent of each other. However in this work but the one switch was used and the one anode. If S_3, S_4, and S_5 are thrown to the left, current can flow from S.B. to B, E, S_3, B_3, along the wire on the back of the disk to R_1, and B_1, then to S_2, through the cell and back to the storage battery, while the brush B_3 is on the sectors connected by the wire. When the last connected sector has passed B_3, the cell is on open circuit until the sector on R_2 connected to R_1 passes under B_2. Current then flows from S.B. to B, E, S_3, O, R, r, B_2, through the connecting wire to R_1, and B_1, then to S_2 and through the cell to the storage battery. It is to be noticed that no matter by which path the current comes to the cell it is in the same direction through it, *i. e.*, from the aluminum to the lead. If there is a counter electromotive force in the cell, the fall of potential over the oscillograph and its resistance must then be equal to the difference between the storage battery voltage and this counter electromotive force. This difference of potential will be registered on the photographic film on the cylinder of the oscillograph.

A flash is registered on the film whenever the small sector on R_2, which is connected to R_1 and R_3, passes under B_2. Then if we rotate B_2 about its axis the resulting flashes on the film will register at exactly corresponding points of the film. Knowing the speed of the motor, we can compute the length of time between any two flashes by measuring the distance between them and comparing with the total film length. One mm. distance between flashes corresponds to 0.00037 sec. when the motor is running at 750 R.P.M. In most cases the flashes are very distinct so that one can measure accurately to 0.0002 sec. If still greater accuracy is desired one has but to increase the speed of the motor.

A calibration curve for the measurement of the voltage recorded by the flashes was made by sending current from a known voltage through the oscillograph and its accompanying resistance when the disk was in rotation. Since the deflections of the oscillograph are proportional to the current through it, they are also proportional to the difference of potential across its terminals. One has but to measure each ordinate and compare it with the deflection from the known source. The value of this ordinate subtracted from the applied voltage gives the counter electromotive force of the cell for that period of open circuit.

If one plots the counter electromotive force as ordinates and the time of open circuit as abscissæ, a curve is obtained which in general appearance resembles the curve of decay of electromotive force in a leaking condenser. But if the equation $V = V_0 e^{-ct}$ is assumed and the value of c computed for several points of the curve, it is found that c is not a

constant throughout the same curve nor the same value in successive curves for the same period of open circuit. It is evident then that this c depends on the time of open circuit and also on the time of closed circuit. But the above formula was derived on the assumption that c is a constant, it is therefore not proper merely to replace c by a function of the times of open and closed circuits. One must go back to initial conditions and construct a formula which will embrace the fact that the counter electromotive force depends both on the time of open circuit and on the time of closed circuit.

THEORY PROPOSED.

Let us assume with Guthe and Schulze that the aluminum anode becomes coated with a layer of some oxide or hydroxide of aluminum and that this solid layer is covered with a very thin film of oxygen gas whose thickness depends on the applied voltage and on the time of open circuit. If this layer of oxygen gas attains a definite thickness for each applied voltage, the thickness of the solid layer must increase with increasing time of closed circuit, for if one places a milliammeter in the circuit with the cell and storage battery, it will be seen that while the current does attain a very low value in a very short time after the circuit is closed, it does not remain at that value but is constantly dropping lower and lower. Even after a whole day on closed circuit, it can be seen that this current is growing smaller, although at a very slow rate. This solid layer is deposited electrolytically, and therefore its thickness must be proportional to the quantity of electricity passing through the cell, which in turn depends on the length of time the cell is left on closed circuit. The drop in counter electromotive force after a period of open circuit is due to the leakage of electricity through the combined thickness of solid layer and oxygen. It has been shown by Schulze that this oxygen film decreases in thickness with increasing time of open circuit. We have here then a clear case of a condenser with a double dielectric, both parts of which leak slightly and change in thickness, the solid layer increasing in thickness with the time of closed circuit and the gas film decreasing in thickness with the time of open circuit.

From the theory of condensers we have

$$i = \frac{-dq}{dt} = \frac{-d(CV)}{dt},$$

where i is the current leaking through the dielectrics, q is the quantity of electricity stored in the condenser, C is the capacity of the condenser at that instant and V is the difference of potential between the two plates. With a double dielectric, we have the formula

$$C = \frac{Sc'c''}{4\pi(c''d' + c'd'')},$$

in which S is the area of the plates, c' is the dielectric constant of the substance whose thickness is d', c'' is the dielectric constant of the substance of thickness d'', and C is the capacity. Dividing both numerator and denominator by c'' and placing $Sc'/4\pi = K$ we have

$$C = \frac{K}{d' + \frac{c'}{c''}d''}.$$

Now let d', c' and d'', c'' apply to the solid layer and gas film, respectively, and call the maximum thickness of the gas film d_0. If we assume the rate of change in thickness of the gas film proportional to the thickness, we have

$$\frac{dd''}{dt} = -cd''; \quad \frac{dd''}{d''} = -c\,dt; \text{ integrating } [\log d'']_{d_0}^{d} = -c[t]_0^t.$$

Therefore $\log d''/d_0 = -ct$ or $d'' = d_0e^{-ct}$. By substitution of this in the equation for i, we get

$$i = \frac{-d}{dt}\frac{KV}{d' + he^{-ct}},$$

where $h = (c'/c'')d_0$.

But the current leaking through a high resistance is equal to the quotient of the electromotive force over the resistance divided by the resistance.

$$i = \frac{V}{r + se^{-ct}},$$

where r equals the resistance of the solid layer and s equals the maximum resistance of the gas film. Equating these two values for i we have

$$\frac{-d}{dt}\frac{KV}{d' + he^{-ct}} = \frac{V}{r + se^{-ct}}.$$

If we carry out the indicated differentiation, separate our variables and integrate from $V = V_0$ when $t = 0$ to $V = V$ when $t = t$ we obtain

$$V = V_0e^{-at}(A + Be^{-ct})^f(C + De^{-ct}),$$

where

$$A = \frac{r}{r+s}, \quad B = \frac{s}{r+s}, \quad C = \frac{d'}{d'+h}, \quad D = \frac{h}{d'+h}, \quad a = \frac{d'}{rK},$$

and

$$f = \frac{\frac{d'}{rc} - \frac{h}{cs}}{-K}.$$

Then

$$a = \frac{d'}{rK} = \frac{d'}{\frac{s'd'}{S}\frac{Sc'}{4\pi}} = \frac{4\pi}{s'c'}$$

and

$$f = \frac{\frac{d'}{rc} - \frac{h}{cs}}{-K} = \frac{\frac{d'}{s'd'c/S} - \frac{h}{s''c'ch/c''S}}{\frac{-Sc'}{4\pi}} = \frac{-4\pi}{s'c'c} + \frac{4\pi c''}{s''c(c')},$$

where s' and s'' are the specific resistances of the solid layer and gas layer, respectively. This s'' must be far greater than s' owing to the nature of the substances. It thus appears that a is very small and that f is negative and smaller even than a. Schulze has given us values for r and s, and also values for d and h. These values substituted in the equations above give $A = 1/51$, $B = 50/51$, $C = 100/101$, and $D = 1/101$. Now assuming that these values are at least of the correct order of magnitude, let us expand $(A+Be^{-ct})^f$ by the binomial theorem. We find

$$(Be^{-ct} + A)^f = B^f e^{-fct} + fB^{f-1}e^{-ct(f-1)}A + \frac{f(f-1)}{2}B^{f-2}e^{-ct(f-2)}A^2 + \cdots.$$

Since f is so extremely small and A is also small, we do not introduce any great error if we neglect all terms after the second. Factoring we have $(Be^{-ct} + A)^f = e^{-fct}(B^f + fB^{f-1}e^{ct}A) = (X - Ye^{ct})$, where $X = B^f$, $Y = -fB^{f-1}A$ and we put $e^{-fct} = 1$ since f is so very small. This simplifies our formula to

$$V = V_0e^{-at}(X - Ye^{ct})(C + De^{-ct}).$$

Expanding and substituting $e^{-at} = 1$, since a is small, we obtain

$$\begin{aligned} V &= V_0(CX - CYe^{ct} + DXe^{-ct} - YD) \\ &= V_0(H - Ge^{ct} + Ke^{-ct}), \end{aligned}$$

which will be shown to fit the curves very closely.

In the above formula c is a constant which must fit all the curves obtained from this cell while H, G, and K are constants for each curve but vary from curve to curve.

To determine these constants we write $v_1 = V_1/V_0$, $v_2 = V_2/V_0$, etc. Then we have

$$\begin{aligned} v_0 &= H - G + K = 1, \\ v_1 &= H - Ge^{ct'} + Ke^{-ct'}, \\ v_2 &= H - Ge^{2ct'} + Ke^{-2ct'}, \\ v_3 &= H - Ge^{3ct'} + Ke^{-3ct'}, \end{aligned}$$

where t' is taken as a certain definite interval of time and we begin to count time from $t = 0$. These equations solved simultaneously give us

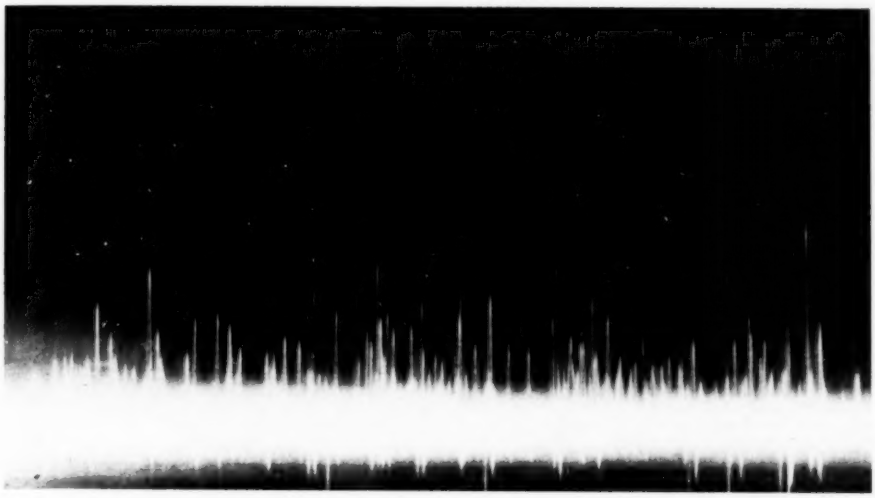

FIG 2.

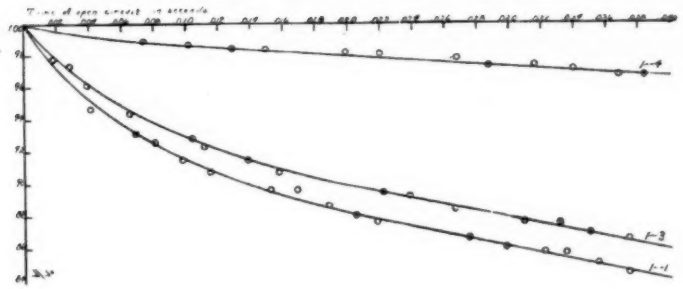

Fig. 3.

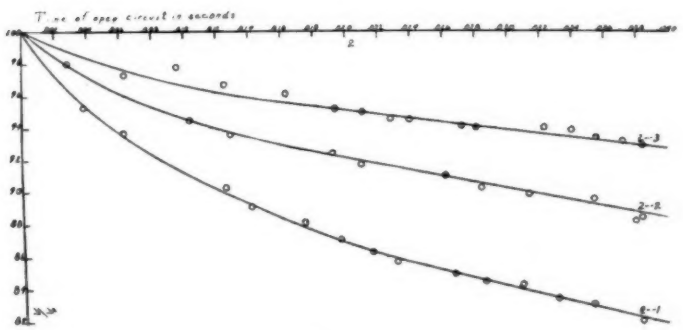

Fig. 4.

ALBERT LEWIS FITCH.

$$K = \frac{(v_3 - v_2) - (v_2 - v_1)e^{ct'}}{(e^{-ct'} - e^{ct'})(e^{-ct'} - 1)},$$

$$G = \frac{(v_3 - v_2) - (v_2 - v_1)e^{-ct'}}{(e^{ct'} - e^{-ct'})(1 - e^{ct'})},$$

$$H = 1 + G - K$$

and

$$\frac{(v_4 - v_3) + (v_2 - v_1)}{(v_3 - v_2)} = e^{-ct'} + e^{ct'} = \text{a constant, } M.$$

Then $e^{2ct'} - Me^{ct'} + 1 = 0$. The solution of this last equation gives us the value of c when we know the values of t' and M. It also shows that M must be a constant for all the curves provided only that we take t' the same. Using t' equal to .0125 sec., the following values are derived for M from six representative curves 3.53, 3.36, 2.96, 3.11, 3.31, and 3.10. The mean value is 3.23 which gives $c = 84$. Likewise using t' equal to .010 sec. we obtain M from the same curves equal to 3.18, 2.87, 2.58, 2.63, 2.75, and 2.93. The mean of these is 2.82 which gives a value of c equal to 88. The mean of these two values of c, 86, was used in all the computation which follows.

1—1.

On closed circuit 16 min.
Applied E.M.F., $V_0 = 99$ volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
$K = .138$, $H = .8629$, $G = .00094$.

1—3.

On closed circuit 3 hrs.
Applied E.M.F., $V_0 = 99$ volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
$K = .121$, $H = .8798$, $G = .00087$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0018	96.9	.978	.981	+3	.0028	96.4	.974	.974	0
.0041	93.8	.947	.959	+12	.0039	95.1	.961	.966	+5
.0069	92.2	.931	.938	+7	.0065	93.5	.944	.948	+4
.0081	91.7	.926	.930	+4	.0104	91.9	.928	.927	−1
.0098	90.6	.915	.920	+5	.0111	91.4	.923	.924	+1
.0115	89.8	.907	.912	+5	.0138	90.6	.915	.914	−1
.0152	88.7	.896	.897	+1	.0157	89.8	.907	.908	+1
.0169	88.7	.896	.891	−5	.0222	88.5	.894	.892	−2
.0188	87.7	.886	.886	−0	.0238	88.3	.892	.889	−3
.0205	87.1	.880	.881	+1	.0266	87.5	.884	.883	−1
.0218	86.7	.876	.878	+2	.0309	86.7	.876	.877	+1
.0275	85.7	.866	.863	−3	.0331	86.6	.875	.872	−3
.0298	85.1	.860	.862	+2	.0350	86.1	.869	.869	−0
.0322	84.8	.857	.857	−0	.0374	85.6	.865	.864	−1
.0335	84.8	.857	.854	−3					
.0355	84.2	.850	.849	−1					
.0374	83.6	.844	.845	+1					

DATA FROM PHOTOGRAPHS.

Since the actual figures are difficult to reproduce but one sample figure will be given. However the measured data will be given for several curves and curves drawn from the data which show the general form of the curves and the rise with time of open circuit.

1—4.

On closed circuit 24 hrs. 15 min.
Applied E.M.F., $V_0 = 99$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0215$, $H = .979$, $G = .00046$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0074	97.9	.989	.989	0
.0102	97.7	.987	.987	0
.0129	97.5	.985	.985	0
.0150	97.4	.984	.983	−1
.0156	97.2	.982	.983	+1
.0199	97.2	.982	.980	−2
.0220	97.1	.981	.979	−2
.0268	96.9	.979	.977	−2
.0287	96.4	.974	.975	+1
.0316	96.4	.974	.973	−1
.0340	96.1	.971	.972	+1
.0368	95.8	.967	.969	+2
.0384	95.8	.967	.967	0

2—1.

On closed circuit 2 min. 30 sec.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .150$, $H = .8515$, $G = .00145$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0038	46.7	.953	.957	+4
.0063	45.9	.937	.937	0
.0126	44.2	.902	.899	−3
.0142	43.6	.890	.891	+1
.0175	43.1	.880	.878	−2
.0197	42.6	.870	.870	0
.0217	42.3	.863	.866	+3
.0232	42.0	.857	.860	+3
.0268	41.6	.850	.852	+2
.0287	41.4	.845	.847	+2
.0310	41.3	.843	.841	−2
.0332	40.8	.834	.835	+1
.0354	40.6	.830	.829	−1
.0384	40.1	.820	.818	−2

2—2.

On closed circuit 9 min. 30 sec.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0945$, $H = .9064$, $G = .00087$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0028	48.0	.980	.980	−0
.0063	47.6	.973	.960	−13
.0104	46.4	.945	.943	−2
.0129	45.9	.936	.935	−1
.0192	45.23	.924	.920	−4
.0210	44.9	.917	.917	−0
.0262	44.57	.910	.908	−2
.0284	44.2	.902	.905	+3
.0314	44.0	.898	.900	+2
.0354	43.86	.895	.893	−2
.0380	43.18	.881	.887	+6
.0384	43.26	.883	.886	+3

2—3.

On closed circuit 1 hr. 32 min.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0568$, $H = .9438$, $G = .000645$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0096	47.85	.978	.967	−11
.0125	47.36	.967	.961	−6
.0163	47.04	.961	.955	−6
.0194	46.70	.952	.951	−1
.0211	46.54	.950	.948	−2
.0228	46.38	.946	.947	+1
.0240	46.38	.946	.946	0
.0272	46.13	.941	.943	+2
.0281	46.05	.940	.942	+2
.0323	46.05	.940	.937	−3
.0340	45.88	.938	.936	−2
.0355	45.72	.933	.933	0
.0372	45.56	.931	.930	−1
.0384	45.48	.928	.928	0

4—1.

On closed circuit 15 min.
Applied E.M.F., V_0 = 100 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .101, H = .9002, G = .00124.

4—2.

On closed circuit on 100 volts 15 min. and on 75 volts 5 min.
Applied E.M.F., V_0 = 75 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .0329, H = .9675, G = .000422.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0058	95.6	.956	.960	+4	.0122	73.3	.978	.978	0
.0098	94.2	.942	.941	−1	.0166	73.1	.975	.974	−1
.0133	92.9	.929	.929	0	.0190	73.1	.975	.972	−3
.0174	91.9	.919	.917	−2	.0219	72.8	.971	.970	−1
.0200	90.8	.908	.911	+3	.0273	72.4	.965	.966	+1
.0233	90.2	.902	.905	+3	.0308	72.0	.960	.964	+4
.0270	89.5	.895	.897	+2	.0332	72.0	.960	.962	+2
.0302	88.8	.888	.891	+3	.0365	72.0	.960	.960	0
.0338	87.8	.878	.883	+5	.0374	72.0	.960	.958	−2
.0374	87.4	.874	.973	−1					

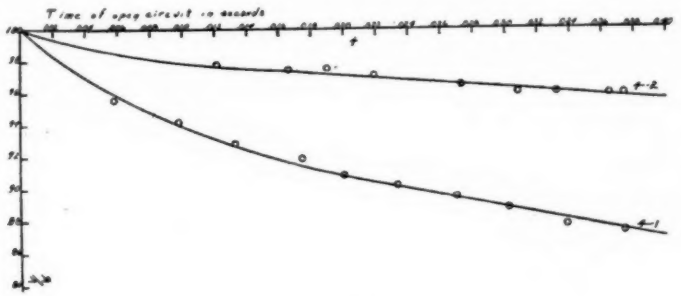

Fig. 5.

5—1.

On closed circuit 1 min.
Applied E.M.F., V_0 = 10 volts.
Counter E.M.F., V.
Time of open circuit t sec.
750 R.P.M.
K = .265, H = .735, G = .00003.

5—2.

On closed circuit 10 min.
Applied E.M.F., V_0 = 10 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .0615, H = .9392, G = .000695.

t.	V	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V	V/V_0 Obs.	V/V_0 Comp.	Error.
.0022	9.16	.916	.955	+37	.0076	9.70	.970	.970	0
.0107	8.20	.820	.840	+20	.0126	9.55	.955	.958	+3
.0142	8.08	.808	.813	+5	.0188	9.52	.952	.948	−4
.0196	7.85	.785	.784	−1	.0218	9.41	.941	.944	+3
.0246	7.78	.778	.767	−11	.0283	9.40	.940	.938	−2
.0307	7.48	.748	.754	+6	.0320	9.34	.934	.932	−2
.0342	7.48	.748	.748	0	.0336	9.34	.934	.930	−4
.0374	6.40	.640	.745	+105	.0365	9.28	.928	.926	−2
					.0374			.934	

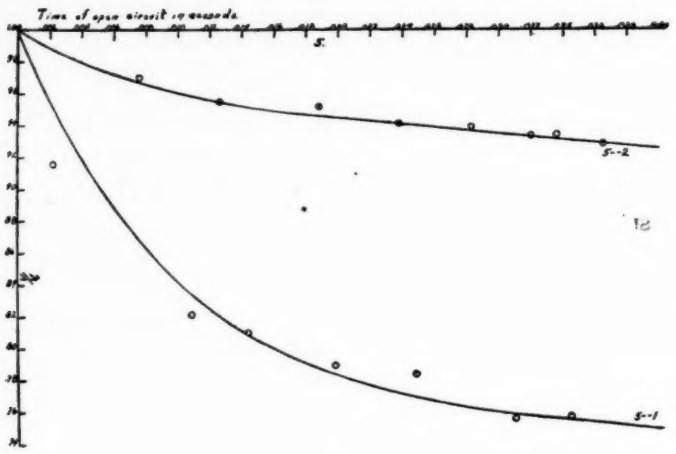

Fig. 6.

DISCUSSION OF FORMULA AND CURVES.

In the foregoing data but a portion of the data taken is given. The curves taken for longer periods of closed circuit lay so close to the axis that accurate measurement is impossible; however they do show the rise of the curve with time of closed circuit.

If one expresses the values of H, G, and K in terms of the thicknesses and resistances of the solid layer and gas film one will find that H should increase, K should decrease, and G should increase with time of closed circuit. The data given show that the H and K fulfill these requirements but that the G actually decreases. This apparent failure of the formula is explained however if we take account of one more term in the binomial expansion.

In every case, the curve of counter electromotive force plotted against time of open circuit rises with time of closed circuit. It seems evident that this counter electromotive force is not due entirely to a gas film as Guthe supposed. It is evident also that a permanent change must take place in the cell with time of closed circuit, for the current which leaks through the cell does not attain a minimum value but is constantly dropping lower and lower. Both of these effects are explained if we assume the cell's action depends upon the thickness of the solid layer which increases in direct proportion to the quantity of electricity passing through the cell, and also upon the thickness of the gas film, which quickly reaches a maximum value for each applied electromotive force and then gradually decreases in thickness with the time of open circuit. The increase in thickness of the solid layer results in an increase in the resistance of the combined layer, which accounts for the gradually

decreasing value of the leakage current on closed circuit and also for the rise of the curves with time of closed circuit. The decreasing thickness of the gas film results in a decrease in the resistance of the combined layer which in turn accounts for the drooping curve.

This way of looking at the cell explains why it acts differently from the ordinary electrolytic cell with both electrodes of some inactive substance, such as platinum. With inactive electrodes, there will be no solid layer deposited; for the electrolytically produced oxygen can not combine with the electrode. In such a cell, the current will drop to a very small value and remain at that value provided the applied voltage is low enough, since the electrodes are unaffected by the passage of the current. But with an aluminum anode there is always deposited some of this solid layer and a drop in current results.

This way of looking at the cell is in accord with the results of Graetz and Pollak, that any electrolyte which will liberate oxygen on electrolysis may be used. It is also in accord with the results of Schulze, that other metals than aluminum may be used, since it only requires that the anode form a compound with the liberated oxygen which has a rather high resistance.

When the cell is used to rectify the alternating current, there is a slight deposit of this solid layer every time the aluminum is the anode. However when the current reverses, this deposit is not decomposed for to decompose the compounds of aluminum by electrolysis a rather high temperature is required. As this process goes on, we may reach a stage where the heat produced in the resistance of this solid film is sufficiently great to raise the temperature of the whole cell to a point where this solid film begins to decompose on the reversal. When this temperature is reached the cell fails to work satisfactorily. This is in accord with the results of others who state that the cell works best at the lower temperatures.

SUMMARY.

1. This investigation has shown that any method of experimentation in which an appreciable length of time must elapse during the taking of data, the cell being on closed circuit with the battery at least a part of this time, will introduce serious errors due to the change taking place in the cell itself.

2. So far as the author is aware, no attempt has ever been made to explain the action of the cell on the theory that the action is due to a double dielectric, one part of which changes with the time of open circuit and the other with time of closed circuit. This investigation has shown such a theory is plausible and fully explains all the cases investigated.

3. The cell does not attain a steady state after a short time of closed circuit, nor does the single dielectric theory seem plausible.

4. The theory leads to the conclusion that any electrolyte which liberates oxygen on electrolysis may be used in the rectifier. It also shows that other metals than aluminum should be available as anodes, since it only requires the metal to form a compound with the liberated oxygen and that this compound have a rather high resistance.

The author is indebted to the University of Michigan for the apparatus provided, to Prof. N. H. Williams for many helpful suggestions, and to Mrs. Fitch for help in the computations.

ANN ARBOR, MICH.,
June 24, 1916.

THE INTENSITY OF X-RAY REFLECTION, AND THE DISTRIBUTION OF THE ELECTRONS IN ATOMS.

BY ARTHUR H. COMPTON.

IN the study of the spectra of X-rays as analyzed by crystal gratings, the remarkably low intensity of the higher orders of reflection has from the first attracted a considerable amount of attention. Preliminary measurements by Mr. W. L. Bragg[1] showed that, when corrected for temperature effects, the intensities of the different orders of reflection of a given X-ray spectrum line are approximately proportional to the inverse square of the order. A more detailed experimental investigation by Professor W. H. Bragg[2] showed that if X-rays of a definite wave-length are reflected at a glancing angle θ by a crystal in which the successive layers of atoms are similar and are similarly spaced, the energy in the reflected beam can be expressed with considerable accuracy by the formula

$$E_r = \frac{C(1 + \cos^2 2\theta)}{\sin^2 \theta} e^{-B \sin^2 \theta}. \tag{1}$$

In this expression C is a constant depending upon the energy in the incident beam, the wave-length of the X-rays, and the nature of the crystal. The factor $e^{-B \sin^2 \theta}$ accounts for the effect of the thermal motion of the atoms. The constant B can be determined experimentally[2] or may be calculated from certain thermal properties of the crystal.[3, 4] The polarization factor $(1 + \cos^2 2\theta)$ was originally deduced by J. J. Thomson[5] for any case of the scattering of X-rays by electrons, and was first introduced into the formula for X-ray reflection by Darwin.[4] Professor Bragg was not able to verify this polarization factor, since in his experiments θ was always small. Using rays of longer wave-length, however, the writer has been able to measure[6] the reflection at sufficiently large glancing angles to obtain an appreciable effect due to this factor, and thus

[1] W. L. Bragg, Proc. Roy. Soc., A, 89, 468 (1914).

[2] W. H. Bragg, Phil. Mag., 27, 881 (1914), also W. H. Bragg and W. L. Bragg, X-rays and Crystal Structure, p. 195.

[3] P. Debye, Ann. d. Phys., 43, 49 (1914).

[4] C. G. Darwin, Phil. Mag., 27, 325 (1914).

[5] J. J. Thomson, Conduction of Electricity through Gases, p. 326.

[6] A. H. Compton, PHYS. REV., 7, 658 (1916).

to verify its existence. Since the sine of the glancing angle is proportional to the order of reflection, this formula includes the result found by W. L. Bragg, but is more general, as it expresses the intensity of the reflection from all possible planes in the crystal.

The theory of the intensity of X-ray reflection has been examined in considerable detail by Mr. C. G. Darwin,[4, 7] who finds that if all the electrons which are effective in scattering the X-rays are close to the centers of the atoms, the energy in the beam reflected at an angle θ should be proportional to

$$\frac{1 + \cos^2 2\theta\, e^{-B \sin^2 \theta}}{\sin \theta \cos \theta}.$$

This expression differs from Bragg's experimental formula by the factor $\tan \theta$, which must be explained, as Darwin pointed out, by the fact that the electrons are not all concentrated near the centers of the atoms, but that at least some of the electrons are at distances from the atomic centers which are of the same order of magnitude as the distance between the atoms. Since the relative intensity of the different orders of X-ray reflection is thus a function of the distribution of the electrons in the atoms of the crystal, it should be possible, knowing the relative intensity of the different orders, to obtain some definite idea of the manner in which these electrons are arranged.

The possibility of finding an arrangement of the electrons which will account in a satisfactory manner for the observed intensity of X-ray reflection at different angles was suggested first by Professor Bragg[8] and independently soon after by the writer.[9] Both of us were able to show the nature of the effect on the intensity of reflection due to certain different distributions of the electrons in the atoms of a crystal grating, but we both neglected to consider certain important factors that must seriously modify the conclusions at which we arrived. We based our arguments on the assumption that the reflected energy would be the same for all orders if all the scattering occurred at the centers of the atoms. This is indeed true for the intensity in the middle of the reflected line, if the crystal acts as a perfect grating, but since the effective width of the spectrum line can be shown to be proportional to $1/\sin \theta \cos \theta$, the reflected energy is reduced in the same ratio. Thus instead of a factor $1/\sin^2 \theta$ there is really, as pointed out above, a factor of only $1/\tan \theta$ to be accounted for by the assumed structure of the atom. In the present paper a more complete theory will be obtained of the dependence

[7] C. G. Darwin, Phil. Mag., 27, 675 (1914).

[8] W. H. Bragg, Bakerian Lecture, March 18, 1915; Phil. Trans., A, 215, 253 (July 13, 1915).

[9] A. H. Compton, Nature, May 27, 1915.

of the intensity of reflection upon the angle and upon the distribution of the electrons in the atoms of the reflecting crystal. The result obtained will be in exact accord with that found in a different manner by Darwin, but will be so expressed that it will be found possible to determine with some definiteness the distribution of the electrons in certain atoms by comparison with the observed intensities of X-ray reflection.

THE INTENSITY OF X-RAY REFLECTION.

Let us therefore obtain a general expression for the energy of a beam of X-rays of wave-length λ which is reflected at a glancing angle θ from a crystal all of whose atoms are similar. For sake of simplicity we may consider the primary beam to be polarized in such a manner that the electric vector is perpendicular to the plane of reflection. This will eliminate the polarization factor $(1 + \cos^2 2\theta)/2$. The temperature factor, $e^{-B \sin^2 \theta}$ may also be neglected if we consider the atoms to be in their positions of rest. These factors can be introduced later into the expression for the intensity of reflection without modifying the rest of the calculation.

Let X-rays thus polarized strike the crystal C (Fig. 1) in the elementary solid angle $d\sigma$ included between $\theta + \epsilon_1$, ϵ_3 and $\theta + \epsilon_1 + d\epsilon_1$, $\epsilon_3 + d\epsilon_3$, and consider the ray reflected at the angle $\theta + \epsilon_2$, ϵ_4. Here θ is the angle

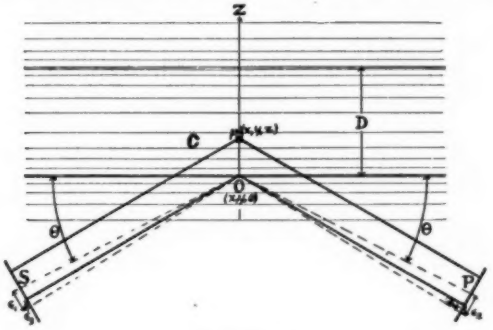

Fig. 1.

of maximum reflection, defined by the relation $n\lambda = 2D \sin \theta$, ϵ_1 and ϵ_2 are small angles measured in the plane of reflection and ϵ_3 and ϵ_4 are similar small angles taken perpendicular to this plane. We shall consider the effect of the reflected ray at the surface of a sphere of very large radius R. If $I_i \cdot d\sigma = I_i \cdot d\epsilon_1 d\epsilon_3$ is the intensity at the surface of the crystal due to this bundle of incident rays, the corresponding amplitude dA_i of the electric vector may be defined by the relation $I_i d\sigma = c(dA_i)^2$. The amplitude at the distance R of the ray scattered by a single electron may then be taken[4, 5] as $(e^2/mC^2R)dA_i$ where e is the charge and m the

mass of the electron, and C is the velocity of light. If the electrons are held very rigidly in position, this expression might have to be slightly modified, but it seems probable that such effects are inappreciable for waves of the frequency of X-rays. The scattering due to the positive nucleus of the atom may be neglected on account of its comparatively great mass.

If we write $\phi = e^2/mC^2$, the amplitude of the reflected ray at the point P $(R, \epsilon_2, \epsilon_4)$ due to a single electron near the surface of the crystal is therefore $(\phi/R) \cdot dA_i$. If $f(z)$ is the volume density of distribution of the electrons at a distance z from the middle plane of a layer of atoms in the crystal, the electric displacement at P at the time t due to a volume element of an atomic layer near the surface of the crystal is therefore

$$f(z)dxdydz \cdot \frac{\phi}{R} dA_i \cdot \cos 2\pi \left(\frac{t}{T} - \frac{\delta + r}{\lambda}\right),$$

where T is the period of vibration, $2\pi\delta/\lambda$ is the phase angle at P due to a crystal element at (x, y, O) at the time $t = 0$, and r is the distance $2z \{\sin \theta + (\epsilon_1 + \epsilon_2) \cos \theta\}$. Neglecting the small term $(\epsilon_1 + \epsilon_2) \cos \theta$, and writing,

$$\beta = 2\pi \left(\frac{t}{T} - \frac{\delta}{\lambda}\right),$$

we find for the displacement at P due to an element of area of a layer of atoms near the surface of the crystal,

$$\frac{\phi}{R} dA_i \cdot dxdy \cdot \int_a^b f(z) \cos \left(\beta - \frac{4\pi z \sin \theta}{\lambda}\right) dz,$$

where $b - a$ is the thickness of the atomic layer, and represents the diameter of the atoms. If N is the number of electrons per unit volume of the crystal, and D is the distance between two successive atomic layers, the number of electrons in unit area of such a layer is ND. The function $f(z)$ may therefore be written $NDF(z)$, where $F(z)$ is the probability that a given electron shall be at a distance z from the mid-plane of the atomic layer to which it belongs. Since the function $F(z)$ can nowhere be greater than at the plane of symmetry, *i. e.*, at $z = 0$, the displacement becomes a maximum when $\beta = 0$. The integral factor of the above expression then becomes,

$$\psi = \int_a^b F(z) \cos \left(\frac{4\pi z \sin \theta}{\lambda}\right) dz,$$

and the amplitude at P due to an element of area of the atomic layer considered may be written

$$\frac{\phi}{R} dA_i \cdot ND \cdot \psi \cdot dxdy.$$

If we consider an element of the crystal so small that the reflection from all of its atomic layers may be considered to be in the same phase, yet containing a large number dn of such layers, the amplitude of the reflected beam at P due to this element is evidently

$$\frac{\phi}{R} dA_i ND\psi dxdy \cdot dn.$$

Or since $dn = dz/D$, the amplitude due to a volume element of the crystal is

$$\frac{\phi}{R} dA_i N\psi dxdydz = dA_0 \cdot dxdydz,$$

where dA_0 is the amplitude of the reflected ray at P per unit volume of the crystal near its surface due to an incident beam of solid angle $d\sigma$.* When the rays are reflected from a depth z below the surface of the crystal, they travel a distance $2z/\sin\theta$ through the crystal before they emerge, so that the intensity is reduced by a factor $e^{2\mu z/\sin\theta}$, where μ is the absorption coefficient. The amplitude is thus reduced by a factor $e^{\mu z/\sin\theta}$, so the amplitude of the beam reflected from any part of the crystal is, per unit volume of the crystal,

$$(2) \qquad dA_r = dA_0 e^{-\frac{\mu z}{\sin\theta}} = dA_i N \frac{\phi}{R} \psi e^{-\frac{\mu z}{\sin\theta}}.$$

Perfect Crystal and Long Trains of Waves.—We shall first determine the energy in the reflected beam on the assumptions (1) that the crystal has no faults, but acts as a perfect grating, and (2) that the X-rays come in trains of waves which are long compared with the depth to which they penetrate the crystal. These are the assumptions on which Darwin's theory of X-ray reflection is based, although he considers also the general nature of the modification to be expected if the crystal is imperfect. On these assumptions reenforcement will occur from all parts of the crystal struck by the rays if all the ϵ's are zero, but when the ϵ's differ from zero the reflections from different parts of the crystal will in general be in different phases. The difference in the path of the ray reflected from an element of the crystal at p $(x, y,$

* It will be noted that this expression seems to make the amplitude of the reflected beam proportional to the number of electrons and hence approximately proportional to the atomic weight of the atoms of the crystal. Though this result is confirmed by some early experiments by Mr. W. L. Bragg,[1] later experiments give different results. In the case of calcite Professor Bragg finds[3] that the *intensity* of the beam reflected by an atom is more nearly proportional to the atomic weight than is the *amplitude*. He writes me that some of his results point one way and some the other. It seems very difficult to obtain a consistent reflection formula on the assumption that it is the intensity which is proportional to the number of electrons. The difficulty is probably to be explained by the nature of the function ψ, for if many of the electrons are at an appreciable distance from the center, the amplitude of the ray scattered by an atom will be considerably less than the sum of the amplitudes due to each electron.

z) and that reflected from an element at O (Fig. 2) is

$$x(\epsilon_2 - \epsilon_1) \sin\theta + y(\epsilon_4 + \epsilon_3) + z\{2 \sin\theta + (\epsilon_1 + \epsilon_2)\cos\theta\},$$

where second order terms in the ϵ's are neglected. The reflected rays

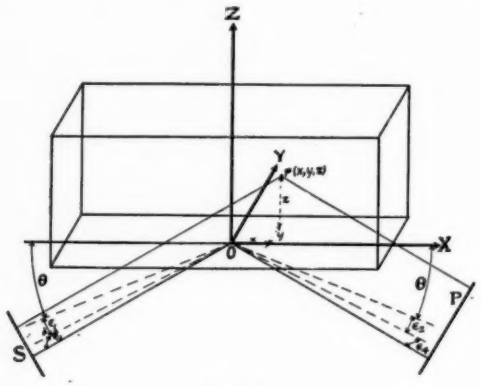

Fig. 2.

from all parts of the crystal are in the same phase when the difference in their paths is $2z \sin\theta$, so the difference in phase between the two reflected beams is

$$\delta = \frac{2\pi}{\lambda}\{x(\epsilon_2 - \epsilon_1)\sin\theta + y(\epsilon_3 + \epsilon_4) + z(\epsilon_1 + \epsilon_2)\cos\theta\}.$$

If the phase angle at P of the ray reflected from the point (o, o, o) is $2\pi\gamma/\lambda$, the displacement due to an element of volume of the crystal at p is, by equation (2),

$$dA_0 e^{-\frac{\mu z}{\sin\theta}} \cdot \cos\frac{2\pi}{\lambda}\{\gamma - x(\epsilon_2 - \epsilon_1)\sin\theta - y(\epsilon_3 + \epsilon_4) - z(\epsilon_1 + \epsilon_2)\cos\theta\}dxdydz.$$

The displacement at P due to the reflection from the whole crystal is therefore

$$dA_0 \int_0^{\infty} dz \int_{-(k/2)}^{k/2} dy \int_{z\cot\theta - l/\sin\theta}^{z\cot\theta + l/\sin\theta} dx \cdot e^{-\frac{\mu z}{\sin\theta}} \cos\frac{2\pi}{\lambda}\{\gamma - x(\epsilon_2 - \epsilon_1)\sin\theta - y(\epsilon_3 + \epsilon_4) - z(\epsilon_1 + \epsilon_2)\cos\theta\},$$

where l is the width and k the length of the slit through which the primary beam passes just before it strikes the crystal. This becomes when integrated,

$$\frac{4dA_0 BC}{gh} \cdot \frac{m\cos\frac{2\pi\gamma}{\lambda} - b\sin\frac{2\pi\gamma}{\lambda}}{m^2 + b^2},$$

where

$$B = \sin\left\{\frac{\pi l}{\lambda}(\epsilon_2 - \epsilon_1)\right\}, \quad C = \sin\left\{\frac{\pi k}{\lambda}(\epsilon_3 + \epsilon_4)\right\},$$

$$g = \frac{2\pi}{\lambda}(\epsilon_2 - \epsilon_1)\sin\theta, \qquad h = \frac{2\pi}{\lambda}(\epsilon_3 + \epsilon_4),$$

$$m = \frac{\mu}{\sin\theta}, \qquad b = \frac{4\pi}{\lambda}\epsilon_2\cos\theta.$$

If this expression is differentiated with respect to γ and equated to zero, it is found that the maximum displacement occurs when

$$\frac{2\pi\gamma}{\lambda} = \tan^{-1}\left(\frac{b}{m}\right),$$

i. e.,

$$\sin\frac{2\pi\gamma}{\lambda} = \frac{b}{\sqrt{m^2 + b^2}}, \quad \cos\frac{2\pi\gamma}{\lambda} = \frac{m}{\sqrt{m^2 + b^2}}.$$

Substituting these values in the above equation, we find for the amplitude of the reflected beam,

$$dA_\epsilon = \frac{4dA_0BC}{gh\sqrt{m^2 + b^2}}. \tag{3}$$

The corresponding intensity of reflection is therefore,

$$dJ_\epsilon = c(dA_\epsilon)^2 = \frac{16c(dA_0)^2B^2C^2}{g^2h^2(m^2 + b^2)},$$

where c has the value assigned above. This may be expanded into the form

$$J_\epsilon d\epsilon_1 d\epsilon_3 = \frac{cl^2k^2}{\sin^2\theta}\cdot\frac{\sin^2\{n(\epsilon_2 - \epsilon_1)\}}{\{n(\epsilon_2 - \epsilon_1)\}^2}\cdot\frac{\sin^2\{p(\epsilon_3 + \epsilon_4)\}}{\{p(\epsilon_3 + \epsilon_4)\}^2}\cdot\frac{A_0^2 d\epsilon_1 d\epsilon_3}{m^2 + g\epsilon_2^2},$$

where $n = \pi l/\lambda$, $p = \pi k/\lambda$, and $q = (4\pi/\lambda)\cos\theta$, and dJ_ϵ and dA_0 are written as $J_\epsilon d\epsilon_1 d\epsilon_3$ and $A_0\sqrt{d\epsilon_1 d\epsilon_3}$ respectively. dJ_ϵ has its greatest value when all the ϵ's are zero, and is then

$$dJ_{(\max)} = \frac{c(dA_0)^2l^2k^2}{\mu^2}.$$

The maximum intensity of the reflected beam is thus independent of θ except for the function dA_0, a result which is in accord with that found by Webster[10] on similar assumptions.

It is not, however, this maximum intensity which is measured in the experiments. It is customary[2, 6] rather to have the opening into the ionization chamber which measures the reflected X-ray beam large enough to receive the rays reflected at all angles ϵ_2 and ϵ_4. If the X-rays come from a point source, the angle ϵ_3 has all values between $-k/2r$ and

[10] D. L. Webster, PHYS. REV., 5, 241 (1915).

$+ k/2r$, where r is the distance from the anticathode to the slit, and ϵ_1 has a range of values $\delta\epsilon_1 = l/r$. The energy per unit time in the reflected beam which is due to the rays incident at angles between ϵ_1 and $\epsilon_1 + d\epsilon_1$ is therefore,

$$E_{\epsilon_1} d\epsilon_1 = \int_{-\infty}^{\infty} R d\epsilon_4 \int_{-k/2r}^{+k/2r} d\epsilon_3 \int_{-\infty}^{\infty} R d\epsilon_2 \cdot J_\epsilon d\epsilon_1.$$

If the crystal is rotated with a constant angular velocity $\omega = d\epsilon_1/dt$, it is exposed to rays incident at the angle ϵ_1 for a time $\delta\epsilon_1/\omega = \delta t$, and the total reflected energy due to the rays incident at the angle ϵ_1 is $E_{\epsilon_1} d\epsilon_1 \cdot \delta t$. If in the time Δt the crystal moves through all angles ϵ_1 at which any appreciable radiation of wave-length λ is reflected, the whole reflected energy is thus,

$$E_r = \delta t \int_{-\infty}^{\infty} E_{\epsilon_1} d\epsilon_1 = R^2 \delta t \int_{-\infty}^{\infty} d\epsilon_4 \int_{-k/2r}^{+k/2r} d\epsilon_3 \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1 \cdot J_\epsilon.$$

Substituting the value of J_ϵ given above, and integrating, this becomes,

$$E_r = \frac{cA_0^2 R^2 l^2 k^3}{r \sin^2\theta} \cdot \frac{\pi^3}{mnpq} \delta t,$$

or

$$E_r = \frac{cl^2 k^2 \lambda^3 \cdot N^2 A_i^2 \phi^2 \psi^2}{2r^2 \omega \mu \sin(2\theta)}. \tag{4}$$

The amplitude dA_i of the beam incident in the solid angle $d\sigma$ has been defined by the relation $c(dA_i)^2 = cA_i^2 d\sigma = I_i d\sigma$, where I_i is the intensity. The energy of the radiation in the solid angle $d\sigma = d\epsilon_1 d\epsilon_3$ which passes through the slit in unit time is therefore $klI_i d\sigma = cklA_i^2 d\epsilon_1 d\epsilon_3$, and as above, putting $\delta\epsilon_1 = l/r$, $\delta\epsilon_3 = k/r$, the total energy which passes through the slit in the time Δt is

$$E_i = klI_i \cdot \delta\epsilon_1 \delta\epsilon_3 \Delta t = \frac{k^2 l^2}{r^2} \cdot cA_i^2 \Delta t.$$

Writing $\Delta\theta = \omega\Delta t$ we find for the ratio of the reflected to the incident energy,

$$R = \frac{E_r}{E_i} = \frac{N^2 \lambda^3 \phi^2 \psi^2}{2\mu \sin 2\theta} \cdot \frac{1}{\Delta\theta}, \tag{5}$$

where $\Delta\theta$ is the angle through which the crystal is turned while making the observations. This result is in accord with that obtained by Darwin, but is worked out for somewhat different experimental conditions.

Imperfect Crystal.—It remains to determine the effect of changing our assumptions. Let us consider the case in which the crystal is not perfect, but is made up of a large number of small crystals, each of which acts as a separate unit. We shall have to determine the energy in the beam reflected by each little crystal, and sum up for all the component crystals.

Each component crystal will for convenience be considered to have the form of a rectangular parallelopiped of dimensions δx, δy, δz. If one of these little crystals is so small that the rays are not appreciably absorbed in passing through it, the phase of the beam reflected from the whole little crystal is the same as that of the ray reflected from its center. In a crystal whose center is at x_1, y_1, z_1 the amplitude contributed by a crystal element at that point is, by equation (2), $e^{-\mu z_1/\sin\theta} dA_0 dx dy dz$. If δ is the phase difference between this ray and the one reflected from the point x, y, z, the amplitude contributed by a crystal element at x, y, z is therefore $e^{-\mu z_1/\sin\theta} dA_0 \cos\delta \cdot dx dy dz$. Substituting the value of δ similar to that used above, we find for the amplitude at P of the beam reflected by the whole little crystal,

$$dA_e' = dA_0 e^{-\frac{\mu z_1}{\sin\theta}} \int_{z_1-(\delta z/2)}^{z_1+(\delta z/2)} dz \int_{y_1-(\delta y/2)}^{y_1+(\delta y/2)} dy \int_{x_1-(\delta x/2)}^{x_1+(\delta x/2)} dx \cdot \cos\frac{2\pi}{\lambda} \times \{(x-x_1)(\epsilon_2-\epsilon_1)\sin\theta + (y-y_1)(\epsilon_3+\epsilon_4) + (z-z_1)(\epsilon_1+\epsilon_2)\cos\theta\}$$

$$= dA_0 e^{-\frac{\mu z_1}{\sin\theta}} \cdot \frac{\sin\left\{\frac{\pi\delta x}{\lambda}(\epsilon_2-\epsilon_1)\sin\theta\right\}}{\frac{\pi\delta x}{\lambda}(\epsilon_2-\epsilon_1)\sin\theta} \cdot \frac{\sin\left\{\frac{\pi\delta y}{\lambda}(\epsilon_3+\epsilon_4)\right\}}{\frac{\pi\delta y}{\lambda}(\epsilon_3+\epsilon_4)} \times \frac{\sin\left\{\frac{\pi\delta z}{\lambda}(\epsilon_1+\epsilon_2)\cos\theta\right\}}{\frac{\pi\delta z}{\lambda}(\epsilon_1+\epsilon_2)\cos\theta} \cdot \delta x\delta y\delta z.$$

As before, the whole energy reflected by this crystal as it is turned through an angle $\Delta\theta$ at an angular velocity ω is given by

$$E_r' = R^2\delta t \int_{-\infty}^{\infty} d\epsilon_4 \int_{-(k/2r)}^{+(k/2r)} d\epsilon_3 \int_{-\infty}^{\infty} d\epsilon_2 \int_{-\infty}^{\infty} d\epsilon_1 \cdot c(A_e')^2.$$

Substituting the above value of $A_e' = dA_e'/d\epsilon_1 d\epsilon_3$ and integrating, we obtain

$$E_r' = \frac{cA_0^2R^2kl\lambda^3 e^{-\frac{2\mu z_1}{\sin\theta}}}{2r^2\omega\sin\theta\cos\theta}\delta x\delta y\delta z.$$

The energy reflected from the whole crystal is of course the sum of the energies reflected from all the component crystals, *i. e.*, $E_r = \Sigma E_{r'}$, or replacing the summation sign by an integral,

$$(4a) \qquad E_r = \int_0^{\infty} dz \int_{-(k/2)}^{+(k/2)} dy \int_{z\cot\theta-(l/2\sin\theta)}^{z\cot\theta+(l/2\sin\theta)} dx \cdot \frac{cA_0^2R^2kl\lambda^3 e^{-\frac{2\mu z}{\sin\theta}}}{2r^2\omega\sin\theta\cos\theta} = \frac{cl^2k^2\lambda^3N^2A_t^2\phi^2\psi^2}{2r^2\omega\mu\sin 2\theta},$$

which is the same as was found in the case of a perfect crystal. Although this result has been obtained from the consideration of one particular type of imperfect crystal, it is evident that the same formula will hold in whatever manner the crystal is divided into its components.

Short Trains of Waves.—It has been pointed out by Webster[10] that if X-rays do not come in long trains like light waves, but come rather in trains which are short compared with the depth to which they penetrate the crystal, the intensity of the reflected beam at the angle of maximum reflection is proportional to $1/\sin^2\theta$. He has since noted, however,[11] that the breadth of the reflected line increases with θ so that the total reflected energy does not obey the same law. The following analysis will show that the total energy reflected in this case is the same as with long trains of waves. If we consider the primary beam to be made up of trains M waves in length, the total number of reenforcing layers is M/n, where n is the order of the reflection. The thickness of the crystal which is effective in reenforcment at any instant is therefore

$$\delta z = \frac{M}{n} D,$$

where D is the distance between two adjacent layers of atoms. If the point x_1, y_1, z_1 is the center of the part of the crystal which has reflected the ray reaching P (R, ϵ_2, ϵ_4) at any particular instant, the amplitude of of the reflected wave at P at that instant is

$$dA_0' e^{-\frac{'\mu z_1}{\sin\theta}} \int_{z_1 \equiv (MD/2n)}^{z_1+(MD/2n)} dz \int_{-(k/2)}^{k/2} dy \int_{z\cot\theta-(l/2\sin\theta)}^{z\cot\theta+(l/2\sin\theta)} dx$$

$$\times \cos\frac{2\pi}{\lambda}\left\{\begin{array}{l}(x-x_1)(\epsilon_2-\epsilon_1)\sin\theta \\ +(y-y_1)(\epsilon_4+\epsilon_3) \\ +(z-z_1)(\epsilon_1+\epsilon_2)\cos\theta\end{array}\right\}$$

$$= dA_0' e^{-\frac{\mu z_1}{\sin\theta}} \cdot \frac{klMD}{n\sin\theta} \cdot \frac{\sin u}{u} \cdot \frac{\sin v}{v} \cdot \frac{\sin w}{w},$$

where

$$u = \frac{\pi l}{\lambda}(\epsilon_2 - \epsilon_1), \quad v = \frac{\pi k}{\lambda}(\epsilon_3 + \epsilon_4), \quad w = \frac{2\pi MD}{n\lambda}\epsilon_2\cos\theta,$$

and the corresponding intensity is

$$c(dA_0')^2 e^{-\frac{2\mu z_1}{\sin\theta}} \frac{k^2l^2M^2D^2}{n^2\sin^2\theta} \cdot \frac{\sin^2 u}{u^2} \cdot \frac{\sin^2 v}{v^2} \cdot \frac{\sin^2 w}{w^2}.$$

Since by hypothesis the primary train of waves is short compared with the depth to which it penetrates the crystal, the length of the reflected train will depend, not on that of the incident one, but only upon the depth

of penetration. In order to find the mean intensity of the reflected beam at this angle, we must therefore integrate this intensity over the whole length of the reflected train, and divide by the average distance between successive trains of waves. If this distance is ρ, the mean intensity of the reflected beam at this angle is thus,

$$\frac{c}{\rho}(dA_0')^2\frac{k^2l^2M^2D^2}{n^2\sin^2\theta}\cdot\frac{\sin^2 u}{u^2}\cdot\frac{\sin^2 v}{v^2}\cdot\frac{\sin^2 w}{w^2}\int_0^\infty e^{-\frac{2\mu z}{\sin\theta}}\cdot 2\sin\theta\, dz$$

$$=\frac{c(dA_0')^2l^2k^2M^2D^2}{\rho n^2\mu}\cdot\frac{\sin^2 u}{u^2}\cdot\frac{\sin^2 v}{v^2}\cdot\frac{\sin^2 w}{w^2}.$$

Since $n\lambda = 2D\sin\theta$, this may be written:

$$J_\epsilon d\sigma = \frac{cM^2\lambda^2k^2l^2(dA_0')^2}{4\rho\mu\sin^2\theta}\cdot\frac{\sin^2 u\sin^2 v\sin^2 w}{u^2v^2w^2}.$$

When $u = v = w = O$, this intensity is a maximum, and the resulting expression agrees with that obtained by Webster. To obtain the whole energy of the reflected beam, however, we must have as before,

$$E_r = R^2\delta t\int_{-\infty}^{\infty}d\epsilon_4\int_{-(k/2r)}^{+(k/2r)}d\epsilon_3\int_{-\infty}^{\infty}d\epsilon_2\int_{-\infty}^{\infty}d\epsilon_1\cdot J_\epsilon,$$

and substituting the above value of J_ϵ this becomes

$$E_r = \frac{cM\lambda^4k^2l^2(A_i')^2N^2\phi^2\psi^2}{2r^2\omega\rho\mu\sin 2\theta}.$$

The mean value of the square of the amplitude of the incident beam is evidently $A_i^2 = A_i'^2\cdot M\lambda/\rho$, so the energy of the reflected beam is as formerly,

$$E_r = \frac{cl^2k^2\lambda^3N^2A_i^2\phi^2\psi^2}{2r^2\omega\mu\sin 2\theta}, \tag{4b}$$

where cA_i^2 now represents the mean intensity of the incident beam instead of its intensity at a given instant.

If there is any difference in the reflecting power of a crystal according to its degree of perfection or the nature of the incident rays, it must therefore be accounted for by a difference in the value of the absorption coefficient μ, since all the other factors in equation (4) have definitely defined values. It has been found by Darwin[7] that the value of this absorption coefficient does differ according to the degree of perfection of the crystal. This results from the fact that a sort of selective absorption occurs near the angle of maximum reflection, which is great only in the case of a crystal that is nearly perfect. Darwin concludes, however, that this effect may be accounted for by inserting a constant factor into

the reflection formula.* We may therefore consider the expression here derived for the energy of the reflected beam of X-rays to hold for any crystal and any beam of X-rays if μ is taken as the *effective* absorption coefficient.

If a beam of X-rays of wave-length λ, polarized so that its electric vector is perpendicular to the plane of incidence, is reflected at an angle θ from a crystal in which all the atomic layers are equally spaced and whose atoms have no thermal motion, the energy in the reflected beam is therefore given by equation (5) as

$$E_r = \frac{E_i}{\Delta\theta} \frac{N^2\lambda^3\phi^2\psi^2}{2\mu \sin 2\theta},$$

where E_i is the whole energy of the radiation of wave-length λ which strikes the crystal as it is turned with uniform angular velocity through an angle $\Delta\theta$, and $\Delta\theta$ is large enough to include all the angles at which rays of wave-length λ are reflected. N is the number of electrons per unit volume of the crystal, μ is the effective absorption coefficient of the X-rays in the crystal at the angle of reflection, and may differ by a constant factor from the coefficient of absorption at other angles. ϕ is the amplitude at unit distance of the ray scattered by a single electron, and has the value e^2/mC^2. ψ is a factor depending upon the arrangement of the electrons in the atomic layers, and has the value

$$\int_a^b F(z) \cos\left(\frac{4\pi \sin\theta}{\lambda} z\right) dz,$$

where $b - a$ is the diameter of an atom, and $F(z)$ is the probability that

* The statement that this correction for selective absorption at the angle of maximum reflection can be accounted for by the insertion of a constant factor into the reflection formula implies that this absorption is equally strong in all orders. Darwin has shown (loc. cit.) that this means a high degree of imperfection of the reflecting crystal. If the crystal is more perfect, the selective absorption must be large compared to the normal absorption and be proportional to $1/\sin 2\theta$. This would make the reflected energy E independent of the angle except for the factor ψ. Darwin considers the fact that the reflected energy at the larger angles is known to fall off rapidly to be sufficient proof that the reflecting crystals cannot be so perfect. It is to be noted, however, that since it is possible, as will be shown below, completely to explain the low intensity of the higher orders by assuming the proper distributions of the electrons in the atoms, the existence of this diminution cannot properly be used to prove the imperfection of the crystal. The fact that the absorption coefficient μ which is to be used in the reflection equation is found by Darwin to be of the same order of magnitude as the normal absorption coefficient indicates, however, that the selective absorption is not large, and hence that the crystal must be very imperfect. The writer has recently made a series of experiments comparing the rate of falling off of the higher orders when tungsten and rhodium rays are reflected from the same crystal. These experiments, which will be published in the near future, indicate rather definitely the existence of the term $\sin 2\theta$ in the denominator of the reflection expression, which would not occur if the crystal used were not sufficiently imperfect to make the absorption coefficient approximately constant.

a given electron will be at a distance z from the mid-plane of the atomic layer to which it belongs. This factor corresponds to the "excess scattering" factor introduced by Darwin.[4] As pointed out above, if the primary beam of X-rays is unpolarized, the factor $\frac{1}{2}(1 + \cos^2 2\theta)$ will have to be introduced, and to account for the thermal motion of the atoms the factor $e^{-B\sin^2\theta}$ must also be included. Introducing these factors, writing $\sin 2\theta = 2 \sin\theta \cos\theta$, and expanding the terms ϕ and ψ, the complete expression for the energy of the reflected beam becomes:

$$E_r = \frac{E_i}{\Delta\theta} \cdot \frac{N^2\lambda^3}{2\mu} \cdot \frac{1 + \cos^2 2\theta}{4 \sin\theta \cos\theta} \left(\frac{e^2}{mC^2}\right)^2 \times \left\{ \int_a^b F(z) \cos \frac{4\pi z \sin\theta}{\lambda} dz \right\}^2 \cdot e^{-B\sin^2\theta}. \tag{6}$$

It may be remarked that this same equation holds when the crystal remains stationary if the angular aperture $\Delta\theta$ of the slit as observed from the anticathode includes all the angles at which X-rays of wave-length λ are reflected.

THE DISTRIBUTION OF THE ELECTRONS IN ATOMS.

By comparing this equation with Bragg's experimental formula (1) it should be possible to determine the form of the function $F(z)$, and hence to find the mean distances of the electrons from the centers of their respective atoms. We shall first attempt a direct solution of the problem, and shall find that there is no possible distribution of the electrons in atoms which will give Bragg's formula as it stands; but a slightly modified form of his law will be found to lead to a definite value of $F(z)$, thus determining the probable distance of an electron from the center of its atom. On comparison with experiment it will be shown, however, that the differences in the intensities of reflection by different crystals are such that no single distribution of the electrons can explain the reflection from all crystals. Arbitrarily chosen distributions which will explain satisfactorily the observed differences between the reflections from certain crystals will then be described, and these will be of considerable interest in connection with certain hypotheses concerning the structure of the atom.

Direct Method.—According to equation (6), if X-rays of wave-length λ are reflected by a certain crystal at two different angles, θ and θ_1, the ratio of the energy in the reflected beam in the two cases is

$$\frac{E}{E_1} = \frac{\dfrac{1 + \cos^2 2\theta}{\sin\theta \cos\theta} \left\{ \int_a^b F(z) \cos\left(\frac{4\pi z \sin\theta}{\lambda}\right) dz \right\}^2 e^{-B\sin^2\theta}}{\dfrac{1 + \cos^2 2\theta_1}{\sin\theta_1 \cos\theta_1} \left\{ \int_a^b F(z) \cos\left(\frac{4\pi z \sin\theta_1}{\lambda}\right) dz \right\}^2 e^{-B\sin^2\theta_1}}. \tag{7}$$

Bragg's experimental formula (1) gives this ratio as

$$\frac{E}{E_1} = \frac{\dfrac{1 + \cos^2 2\theta}{\sin^2 \theta}}{\dfrac{1 + \cos^2 2\theta_1}{\sin^2 \theta_1}} \frac{e^{-B \sin^2 \theta}}{e^{-B \sin^2 \theta_1}} \tag{8}$$

and on comparing these two expressions, we find

$$\frac{\left\{\int_a^b F(z) \cos\left(\frac{4\pi z \sin \theta}{\lambda}\right) dz\right\}^2}{\left\{\int_a^b F(z) \cos\left(\frac{4\pi z \sin \theta_1}{\lambda}\right) dz\right\}^2} = \frac{\tan \theta_1}{\tan \theta}. \tag{9}$$

Extracting the square root, and substituting

$$x = \frac{4\pi \sin \theta_1}{\lambda} z, \quad \phi(x) = F\left(\frac{\lambda x}{4\pi \sin \theta_1}\right) = F(z),$$

$$\alpha^2 = \frac{\tan \theta}{\tan \theta_1}, \qquad \beta = \frac{\sin \theta}{\sin \theta_1},$$

$$r = \frac{4\pi \sin \theta_1}{\lambda} a, \qquad s = \frac{4\pi \sin \theta_1}{\lambda} b,$$

this equation may be reduced to the form

$$\int_r^s \phi(x) \{\alpha \cos(\beta x) \pm \cos x\} dx = 0. \tag{10}$$

From this equation we have to evaluate the function $\phi(x)$ and the limits of integration, r and s.

This seems to be a difficult form of integral equation to attack by direct mathematical methods. It is possible by graphical methods to show that there are an infinite number of solutions of the form $\phi(x) = c \sin px$, if $r = -s$, where the constants c and p can have any value. These solutions, however, imply that the probability function ϕ becomes negative at certain points, which is meaningless, so that they do not apply to this problem. There are also an infinite number of solutions of the type

$$\phi(x) = c_1 \sin^n p_1 x + c_2 \cos^m p_2 x + c_3,$$

if p_1 and p_2 are integers, r and s are integral multiples of π, β is an integer, c_1, c_2, n, m, may have any value, and c_3 is large enough to prevent the expression from becoming negative. Experiment shows, however, that β is not necessarily an integer, so that these solutions also do not apply. Other possible solutions are not obvious.

The necessary form of the function $F(z)$, and hence also of the function

$\phi(x)$ can be found, however, by certain physical considerations. If we consider the primary beam of X-rays to be plane polarized, and the reflecting crystal to be at a very low temperature, the experimental law expressed in equation (8) becomes $E/E_1 = \sin^2\theta_1/\sin^2\theta$. The ratio of the intensity of the reflected beam at two different angles thus depends only upon the angles at which reflection occurs, and is independent of the wave-length of the reflected beam. Thus with the layers of atoms at a distance a apart and with a beam of X-rays of wave-length λ, the ratio of the reflected energy at the two angles θ and θ_1 is the same as when the layers are at a distance ma apart using X-rays of wave-length $m\lambda$. Since, however, the ratio of these intensities is determined by the distribution of the electrons in the atomic layers, this means that this distribution shall be the same on the scale ma as it is on the scale a. That is, if the density of distribution is p times as great at $z = (1/q)a$ as at $z = (n/q)a$, it must be also p times as great at $z = (1/q)(ma)$ as at $z = (n/q)(ma)$, or

$$p = \frac{F\left(\frac{1}{q}a\right)}{F\left(\frac{n}{q}a\right)} = \frac{F\left(\frac{1}{q}ma\right)}{F\left(\frac{n}{q}ma\right)},$$

and in general

$$\frac{F(z)}{F(nz)} = \frac{F(mz)}{F(nmz)}, \tag{11}$$

where the constants n and m may have any value. The only type of function which will satisfy this relation may be shown to be

$$F(z) = b_1 z^{-p} \qquad [z > 0]$$
$$= b_1(-z)^{-p} \quad [z < 0],$$

where b_1 and p are arbitrary constants. Since

$$z = \frac{\lambda x}{4\pi \sin\theta_1},$$

$$\phi(x) = F(z) = b_1\left\{\frac{\lambda x}{4\pi \sin\theta}\right\}^{-p} = bx^{-p} \quad [x > 0]. \tag{12}$$

Equation (11) shows that the density of distribution of the electrons can vanish nowhere unless it is everywhere zero, so the limits of integration of equation (10) must be $-\infty$ and ∞. This of course corresponds to an atom with an infinite radius.

Substituting this value for $\phi(x)$, and remembering that the function under the integral sign is symmetrical on both sides of the plane $z = 0$,

equation (10) may be written

$$\int_0^\infty x^{-p}\{\alpha \cos \beta x \pm \cos x\}dx = 0 \tag{13}$$

The integral is a known one,[12] the solution being

$$\begin{aligned} &(\alpha\beta^{p-1} \pm 1)\frac{\pi}{2\Gamma(p)} \sec\left(\frac{p\pi}{2}\right) && \text{for } [0 < p < 1] \\ &\infty && \text{for } [p \gtrless 1] \\ &\text{indeterminate} && \text{for } [p \lesseqgtr 0]. \end{aligned}$$

This integral can vanish only when

$$\alpha\beta^{p-1} \pm 1 = 0$$

or

$$\frac{\cos\theta}{\cos\theta_1} = \left\{\frac{\sin\theta}{\sin\theta_1}\right\}^{2p-1}.$$

Since θ and θ_1 can have any values, it is obvious that there is no constant value of p which will satisfy this equation. Thus there is no solution of the integral equation (10) which meets the conditions. We must conclude, therefore, that there is no possible distribution of the electrons in the atomic layers which will give Bragg's experimental law as it stands.*

If equation (1) is modified by inserting the factor $\cos\theta$ in the denominator, its value is not greatly changed, since θ is usually small. This modification changes the quantity on the right-hand side of equation (9) to $\sin\theta_1/\sin\theta$, and the coefficient α in equations (10) and (13) becomes $(\sin\theta/\sin\theta_1)^{1/2}$, the other quantities remaining unchanged. In this case the left hand side of equation (13) vanishes only when

$$\frac{\sin^{1/2}\theta}{\sin^{1/2}\theta_1} \cdot \left\{\frac{\sin\theta}{\sin\theta_1}\right\}^{p-1} = 1,$$

or

$$p = \tfrac{1}{2}$$

(14) whence

$$\begin{aligned} F(z) &= b_1 z^{-1/2} && [z > 0] \\ &= b_1(-z)^{-1/2} && [z < 0]. \end{aligned}$$

Thus although Bragg's law in its original form is not given by any possible

[11] D. L. Webster, PHYS. REV., 7, 696 (1916).

[12] Bierens de Haan, Nouv. Tables d'integrales definies.

* On somewhat different assumptions from those used here, Professor Bragg has found a distribution of the scattering material which leads to the law $E/E_1 = n_1^2/n^2$, where n is the order of reflection.[8] The distribution he finds is, however, a function of the distance between the atomic layers, and so cannot truly represent the arrangement of the electrons in the atoms. In fact it is possible to show by reasoning similar to that used above that on his assumptions also there is no distribution of the electrons which will give his law for the intensity of reflection.

distribution of the electrons, it can be obtained in a slightly modified form if the density of distribution of the electrons is inversely proportional to the square root of the distance from the mid-plane of the atomic layer to which they belong.

The quantity $F(z)$ represents the probability that a given electron shall be at a distance z from the middle of its layer of atoms at any instant. It is evident, therefore, that the relation $\int_{-\infty}^{\infty} F(z)dz = 1$ or $\int_{0}^{\infty} F(z)dz = \frac{1}{2}$ must be satisfied. The constant b_1 in equation (12), representing the probability $F(z)$ at unit distance from the mid-plane is thus defined by the expression

$$b_1 \int_0^{\infty} z^{-p}dz = \tfrac{1}{2},$$

or

$$b_1 = 0,$$

since

$$\int_0^{\infty} z^{-p}dz = \infty$$

for all values of p. This means that there can be no appreciable density of distribution of the electrons in the atomic layer unless there are an infinite number of electrons in it. It is evident therefore that the function $F(z)$ cannot have the form $b \cdot z^{-p}$. According to the argument above, this means that the relative intensity of the beam of X-rays reflected at different angles must depend not only upon the angle of reflection, but also upon the wave-length of the incident beam of X-rays.

Empirical Method.—Since there is no possible distribution of the electrons in the atoms which will give a law of reflection of the form of Bragg's empirical expression, let us see if it is not possible to find some arbitrary distribution which will give a reflection formula fitting the experimenral data better than his law. In order conveniently to compare data obtained with different crystals and with X-rays of different wave-lengths, let us remember, according to equation (7), that the part of the ratio E/E_1 which is due to the diffuseness of the atomic planes is

$$U^2 = \frac{\left\{\int_a^b F(z)\cos\left(\frac{4\pi z \sin\theta}{\lambda}\right)dz\right\}^2}{\left\{\int_a^b F(z)\cos\left(\frac{4\pi z \sin\theta_1}{\lambda}\right)dz\right\}^2} = \frac{\psi^2}{\psi_1^2} = \frac{E}{E_1}\cdot\frac{\frac{1+\cos^2 2\theta_1}{\sin\theta_1\cos\theta_1}}{\frac{1+\cos^2 2\theta}{\sin\theta\cos\theta}}\cdot\frac{e^{-B\sin^2\theta_1}}{e^{-B\sin^2\theta}}.$$

From any assumed distribution of electrons $F(z)$ the theoretical values of

(15) $$U = \frac{\psi}{\psi_1}$$

may be calculated for different angles of reflection, and by comparison with the corresponding experimental values as given by the equation

$$(16) \qquad U = \left\{ \frac{E}{E_1} \cdot \frac{\frac{1 + \cos^2 2\theta_1}{\sin \theta_1 \cos \theta_1}}{\frac{1 + \cos^2 2\theta}{\sin \theta \cos \theta}} \cdot \frac{e^{-B \sin^2 \theta_1}}{e^{-B \sin^2 \theta}} \right\}^{1/2},$$

the accuracy of the assumed distribution may be tested.

For the cases of rock-salt and calcite the values of E/E_1 have been determined experimentally by Professor Bragg.[2, 8] His results are given in Tables I. and II., columns 3. In the case of calcite the reflection at

TABLE I.

Rock-Salt.

Crystal Face.	$\frac{\sin \theta}{\sin \theta_1}$.	$\frac{E}{E_1}$.	U_{obs}.	U_{calc_1}.	U_{calc_2}.
100	1.00	1.00	1.00	1.00	1.00
110	1.41	.41	.79	.83	.81
111	1.73	.244	.69	.75	.695
100	2.00	.187	.67	.70	.63
110	2.83	.0705	.55	.58	.56
100	3.00	.0625	.55	.56	.55
111	3.46	.042	.54	.51	.50

TABLE II.

Calcite.

Crystal Face.	$\frac{\sin \theta}{\sin \theta_1}$.	$\frac{E}{E_1}$.	U_{obs}.	U_{calc_1}.	U_{calc_2}.
$1\bar{1}1$	.80	1.44	1.05	1.12	1.03
100	1.00	1.12	1.03	1.00	1.00
111	1.07	.95	.98	.97	.98
$1\bar{1}0$	1.24	.67	.88	.90	.95
110	1.59	.46	.86	.78	.87
$1\bar{1}1$	1.60	.48	.88	.78	.87
100	2.00	.257	.72	.70	.79
211	2.12	.286	.78	.68	.76
111	2.14	.297	.80	.68	.76
$1\bar{1}0$	2.46	.164	.65	.62	.69
100	3.00	.113	.61	.56	.60
110	3.22	.091	.57	.54	.58
$1\bar{1}1$	3.21	.108	.62	.54	.58
100	4.00	.034	.41	.48	.44
111	4.28	.036	.42	.46	.42
110	4.78	.021	.37	.43	.36
$1\bar{1}0$	4.91	.013	.30	.42	.35

different angles is produced by layers of different kinds of atoms, but the values here given have been corrected according to the method explained by Professor Bragg[8] for the effect of the differences in the atomic layers, so these figures may be taken as due to a crystal all of whose atoms are similar and whose atomic layers are uniformly spaced. In these tables θ_1 is taken as the angle of the first order reflection from the (1, 0, 0) face of the crystal. The values of U calculated from the observed values of E/E_1 are given in columns 4, and are plotted in Fig. 3 against the corresponding values of $\sin\theta/\sin\theta_1$.* The open circles in this figure represent the experimental values of U for rock-salt, and the solid ones for calcite. The agreement between the results of successive experiments indicates that these data may be taken as accurate within a probable error of about one or two per cent., although consistent errors of considerably greater magnitude may occur due to various causes.

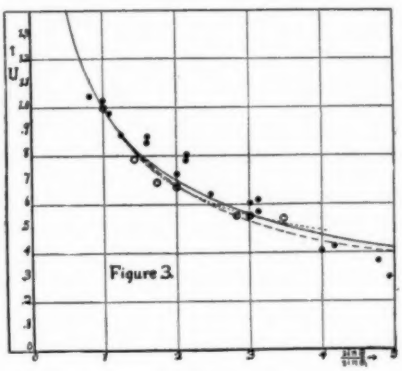

Fig. 3.

The values of U calculated from Bragg's law, equation (1), are given in columns 5 of the tables and are shown on Fig. 3 by the solid line. If the function $F(z)$ is assumed to have the form bz^{-p}, U has the values observed for the first and second order reflections from rock-salt when

* In calculating the values of U here given, the constant B in equation (16) has been evaluated by Debye's formula,[3]

$$B = \frac{1.142 \times 10^{-12}}{A\Theta\lambda^2}\frac{\phi(x)}{x},$$

where A is the atomic weight, Θ is Debye's "characteristic temperature," $x = \Theta/T$, where T is the absolute temperature, and $\phi(x)$ is a function which Debye evaluates. The value of B thus calculated has been found by Bragg[2] to account with considerable accuracy for the observed changes of the intensity of reflection with temperature. For rock-salt $\Theta = 260°$ K., $A = 29$, $x = .89$, $\phi = .80$, and using rhodium rays of wave-length $\lambda = .614 \times 10^{-8}$ we obtain $B = 3.6$. In the case of calcite $\Theta = 910°$ (determined from the specific heat at 298° K.), and taking $A = 20$, $x = 3.10$ and $\phi = .473$ we find $B = 0.25$. It is these values which have been used in calculating U. If a "Nullpunktsenergie" is assumed, Debye shows that the value of B is

$$B = \frac{1.142 \times 10^{-12}}{A\Theta\lambda^2}\left(\frac{\phi(x)}{x} + \frac{1}{4}\right).$$

In this case for rock-salt $B = 4.6$ and for calcite $B = .67$. This makes no very large difference in the values of U. In any case the effect of the temperature factor is not large at the angles at which these measurements are made, so that any slight error in the value of B will not greatly affect the results.

$p = 0.425$, which gives $U = (\sin\theta_1/\sin\theta)^{.575}$. This expression is plotted in the broken line of Fig. 3, and is about as accurate an expression for the reflected energy as can be obtained with this type of function. Professor Bragg has suggested[8] the use of a function of the form $F(z) = be^{-cz}$ to express the distribution of the electrons. The coefficient b in this case has a fiinte value, so although this function also implies an atom of infinite radius it is not *a priori* impossible. It can be shown, however, that the values of U obtained with such a distribution are considerably too large at moderately small angles, and decrease much too rapidly at large angles. Better agreement is obtained if a distribution of this type is combined with a certain concentration $F(O) = a$ of the electrons at the middle of the reflecting layers. In this case

$$U = \frac{a/b + c\Big/\left\{c^2 + \left(\frac{4\pi \sin\theta}{\lambda}\right)^2\right\}}{a/b + c\Big/\left\{c^2 + \left(\frac{4\pi \sin\theta_1}{\lambda}\right)^2\right\}}.$$

In order to make the values of U thus calculated agree with the observed values for the second and third orders of reflection from rock-salt we must put $a/b = 0.274\,\lambda$ and $c = 1.51/\lambda$. The values of U thus obtained are plotted in the dotted curve of Fig. 3, and are seen to be in better agreement with the experiments on rock-salt than is the empirical law expressed by the solid curve. A comparison of the experimental data for rock-salt and calcite as shown in Fig. 3 shows at once that a curve which corresponds to the observed values of U for rock-salt cannot fit accurately the data for calcite. Professor Bragg has suggested[8] the possibility of the existence of such a difference, but it was a difficult thing to detect on account of the many disturbing factors. Since by equation (15) U is a function only of the distribution of the electrons in the atomic layers and of $\sin\theta/\lambda$, any observed differences in U for a given value of $\sin\theta/\lambda$ can be explained only by differences in the distributions of the electrons in the layers of atoms which do the reflecting. Thus we may conclude that the distribution is not the same in the atoms of calcite as it is in the atoms of rock-salt.* It appears, therefore, that

* Note added December 9, 1916: A more striking example of the difference in the value of U for different crystals is afforded by Vegard's recent determination of the intensity of X-ray reflection from silver (Phil. Mag., 32, 94, July, 1916). He finds the intensity of the first three orders of reflection from the (111) plane to be in the ratio of 1.00 : 0.45 : 0.11, respectively. The corresponding values of U are 1.00 : 1.03 : 0.73. In the case of rock-salt we have found the values of U for the first three orders of reflection from the (100) plane to be 1.00, 0.67 and 0.55. The difference is too great to be accounted for by experimental error. Since, as pointed out above, U depends only upon the distribution of the electrons in the atoms of the crystal, these differences must be taken as a strong confirmation of our

instead of considering the electrons to be distributed according to some general law such as we have been discussing, one should rather consider every atom to possess a finite number of electrons, each placed at a definite distance from its center.

Atoms with a Finite Number of Electrons.—If each atom of a certain kind has an electron at a distance a from its center, the average effect from a large number of such atoms will be the same as that due to a uniform distribution of the electrons over the surface of a sphere of radius a. The center of this equivalent spherical shell will be in the mid-plane of the atomic layer, and the probability that a given electron in the shell will be at a distance z from the middle of the layer may be shown to be

$$F(z) = c \quad [-a < z < a],$$

or, in virtue of the relation

$$\int_{-a}^{a} c\,dz = 1,$$

$$F(z) = \frac{1}{2a}\,[-a < z < a].$$

The value of ψ due to an electron in such a shell is therefore

$$\psi' = \frac{1}{2a}\int_{-a}^{a} \cos\left(\frac{4\pi z \sin\theta}{\lambda}\right) dz = \frac{\sin\left(\frac{4\pi a \sin\theta}{\lambda}\right)}{\frac{4\pi a \sin\theta}{\lambda}}, \tag{17}$$

and the value of ψ for a whole atom is

$$\psi = \frac{1}{\nu}\sum_{r}\psi_r' = \frac{1}{\nu}\sum_{r}\sin\left(\frac{4\pi a_r \sin\theta}{\lambda}\right)\Big/\left(\frac{4\pi a_r \sin\theta}{\lambda}\right), \tag{18}$$

where ν is the number of electrons in the atom, and the summation extends over all the r's from 1 to ν. In any actual case this summation is most readily performed by plotting ψ' according to equation (17) and taking off its values corresponding to the desired values of $a \sin\theta/\lambda$. From the value of ψ thus obtained, the quantity U can be calculated as before by equation (15).

Attempts to obtain a suitable formula for U by thus adding the effects of a number of electrons placed at arbitrary distances a from the centers

fundamental assumption that the intensity of X-ray reflection depends upon the distribution of the electrons in the atoms of the reflecting crystal. If the values of U for silver are calculated on the basis of the assumptions used below in the case of calcite, giving to each electron an angular momentum of h/π, we obtain the values of U for the first three orders of reflection as 1.00 : 0.93 : 0.82. Though the agreement is far from perfect, it is much better than that obtained with the values 1.00 : 0.70 : 0.56, assigned by Bragg's law.

of the atoms soon convince one that the form of the resulting curve is very sensitive to changes in the assumed values of a. The results obtained above indicate that there must be a rather strong concentration of the electrons near the centers of the atoms, but it is difficult to select a distribution of the outer electrons which will give a reflection formula that agrees with the experimental data.

In the case of calcite it was found that a fairly acceptable expression could be obtained if the atoms of calcium, carbon and oxygen were assumed to have a number of electrons equal to their positive valence, *i. e.*, 2, 4 and 6, respectively, placed at distances from the centers of the atoms inversely proportional to the valence, together with an arbitrary number of electrons placed at the centers of the atoms. The use of this number of electrons in the outer part of each atom was suggested by well-known theories of valence, while some such spacing as this seemed necessary in order to obtain a suitable formula for U. This assumption concerning the spacing is, however, very nearly what is to be expected if these valency electrons revolve in rings about the centers of their respective atoms, all the electrons having the same angular momentum. For according to classical mechanics,[13] the centrifugal force $m\omega^2 a$, where m is the mass and ω the angular velocity of the electron and a is the radius of its orbit, must be balanced by the centripetal force $(M - \sigma_n)e^2/a^2$ where e is the electronic charge, M is the total charge in electronic units on the part of the atom inside the ring considered, and σ_n is a term which depends upon the mutual repulsion between the electrons in the same ring. With one electron in the ring $\sigma_1 = 0$, for two $\sigma_2 = .25$, and similarly $\sigma_4 = .96$, $\sigma_6 = 1.83$, $\sigma_7 = 2.31$ and $\sigma_8 = 2.81$. But if the angular momentum is constant, *i. e.*, $ma^2\omega = c$, we may write

$$ma \cdot \frac{c^2}{m^2 a^4} = \frac{e^2}{a^2}(M - \sigma_n),$$

or

$$a = \frac{c^2}{me^2} \frac{1}{(M - \sigma_n)}. \tag{19}$$

Since for the outer ring of a neutral atom M is equal to the number of electrons in the ring, a is thus approximately inversely proportional to the number of valency electrons. This suggested, therefore, the assumption of the constancy of the angular momentum of the electrons in the atoms as a working basis.

It is of course possible to find any number of satisfactory arrangements unless the number of electrons in the atoms is defined. Barkla has shown[13] that the number of electrons in an atom which are effective in

[13] H. G. J. Moseley, Phil. Mag., 26, 1032 (1913).

scattering X-rays is approximately equal to half the atomic weight. His work in connection with that of Rutherford on the scattering of alpha particles[15] and of Moseley on the high frequency spectra of the elements[14] makes it very probable that if N is the atomic number, there are N electrons distributed about the atomic nucleus, and that all these electrons are effective in scattering X-rays. This, together with the assumption used above concerning the valency electrons, determines the number of electrons in both rings of the first row of elements in the periodic table, including carbon and oxygen. For the second and third rows it has been assumed, in accordance with Moseley's interpretation of his X-ray spectra,[13] that the inner ring contains 4 electrons. This leaves 6 electrons in the middle ring of the second row of atoms. There remain 8 electrons to be placed in the calcium atom, and it seemed reasonable to put these in a ring just inside of the valency electrons.

With the number of electrons in each ring thus determined, the relative distance of each electron from the nucleus can immediately be

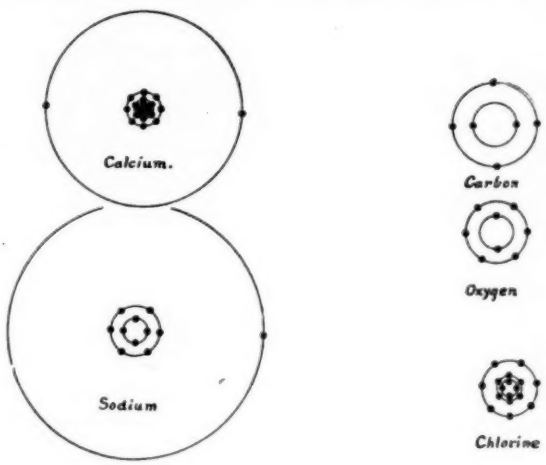

Fig. 4.

calculated by equation (19), and the corresponding values of U can be determined by equations (15) and (18). If the angular momentum of all the electrons is the same, their relative spacing in the atoms here used is as shown in Fig. 4. The value of U obtained for calcite on the basis of these assumptions is shown in the dotted curve of Fig. 5. Although the agreement is fair, it is evident that the theoretical values are too high in the low orders, and fall off too rapidly in the higher orders. It is to be noted that as there is but a single arbitrary constant, the

[14] C. G. Barkla, Phil. Mag., 14, 408 (1907).

[15] E. Rutherford, Phil. Mag., 27, 488 (1914).

angular momentum of an electron, in the equation for U, even this general agreement indicates that we are working along the right line. If the assumptions are modified to the extent of giving the electrons in the inner rings and in the second calcium ring half the angular momentum of those in the outer rings, the values of U given in column 6 of Table II. and shown in the solid curve of Fig. 5 are obtained. The equation for ψ is in this case,

$$\psi = \frac{1}{50}\left\{\begin{array}{l}\left[\begin{array}{l}4\sin(.013k\sin\theta)/.013k\sin\theta+6\sin(.018k\sin\theta)/.018k\sin\theta \\ +8\sin(.139k\sin\theta)/.139k\sin\theta+2\sin(.571k\sin\theta)/.571k\sin\theta\end{array}\right] \\ +[2\sin(.043k\sin\theta)/.043k\sin\theta+4\sin(.329k\sin\theta)/.329k\sin\theta] \\ +3[2\sin(.032k\sin\theta)/.032k\sin\theta+6\sin(.240k\sin\theta)/.240k\sin\theta]\end{array}\right\}.$$

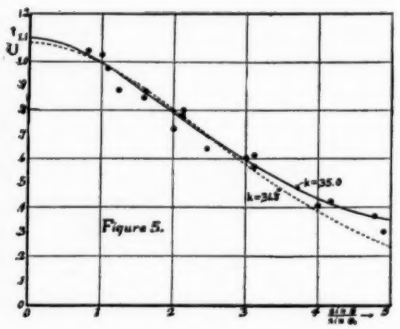

Fig. 5.

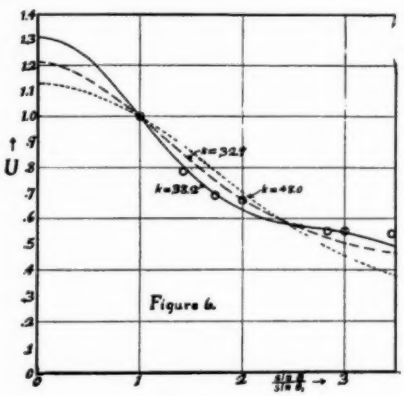

Fig. 6.

50 is the number of electrons in a molecule of calcium carbonate, and k is the constant $(4\pi/\lambda)\cdot(c^2/me^2)$ where c is the angular momentum of an electron in one of the outer rings. The agreement of the theoretical curve with the observed values is well within the probable experimental error, and is evidently better than that obtained with Bragg's empirical formula.

If the assumption that all the electrons have the same angular momentum is used in the case of rock-salt, a result is obtained which does not at all correspond with the observed intensities of reflection, as is shown in the dotted curve of Fig. 6. In order to account for the low value of U around the second order, it seems necessary that there shall be a ring of electrons about 1.00×10^{-8} cm. in radius which contains a considerable number of electrons, and that there shall be no other heavy ring of more than half as great diameter. This arrangement is obtained if we consider the electrons in the outer rings of chlorine to have 3/2 as great angular momentum as those of sodium, and if, as before, we assume the

inner ring of each atom to have $\frac{1}{2}$ the normal angular momentum. According to the work of J. J. Thomson[16] it appears probable that the valency electron of sodium goes over to the chlorine atom and becomes a part of its outer ring. This would give 8 electrons in the outer ring of chlorine and none in that of sodium. The values of U given in Table I. and shown in the solid curve of Fig. 6 have been calculated on this basis. If the valency electron of sodium is not thus transferred, the broken curve in this figure is obtained on the same assumptions concerning angular momentum. It will be seen that the former hypothesis yields the better results. Although the accuracy of the experimental values of U is not great enough at present to warrant any definite conclusions concerning such details, the difference in the curves obtained by thus shifting the position of a single electron indicates the extreme sensitiveness of this method for determining the distribution of the electrons in atoms.

CONCLUSIONS AND DISCUSSION.

Thus we see that if certain definite distributions of the electrons in atoms are assumed, it is possible to explain in a satisfactory manner the rapid decrease in the intensity of the higher orders of reflection of X-rays by crystals. Although it is not possible thus to derive Bragg's empirical formula, expressions for the intensity of reflection can be derived which agree better with experiment than does his law. We have shown from a theoretical standpoint that any equation which is to express adequately the relative intensity of the beam of X-rays reflected at different angles must be a function not only of the angle of reflection, as is Bragg's law, but must involve also the wave-length of the incident beam of X-rays. Professor Bragg has suggested that the observed values of the intensities of the reflection from different crystals actually show differences which do not depend upon the angle alone. These differences are usually masked by the large general variations of the intensity with the angle of reflection which is to be expected with any crystal grating; in the cases of rock-salt and calcite, however, these general variations can be accounted for, and it has been found above that there remain certain decided differences between the spectra from these crystals. It has been shown theoretically that any such differences must be due to differences in the distribution of the electrons in the atoms of the respective crystals, and the arrangements of the electrons which have been assigned to the different atoms have been found capable of accounting for these variations. Thus our fundamental hypothesis that the intensity of the reflected beam is a function of this distribution is strongly confirmed.

[16] J. J. Thomson, Phil. Mag., 27, 757 (1914).

The scarcity and comparative uncertainty of the experimental data make it premature to arrive at any positive conclusions concerning the details of the distribution of the electrons in the atoms considered. In general, however, it may be said that a comparison of the different distributions of the electrons which have been found to give satisfactory results show that there is usually a rather strong concentration of the electrons near the centers of the atoms, but with a considerable number at appreciable distances from the atomic centers. The expression $F(z) = bz^{-\frac{1}{2}}$, which was found to give Bragg's law in a slightly modified form, implies that the volume of density of distribution of electrons is inversely proportional to the 5/2 power of the distance from the center of the atom, and the satisfactory distributions in the case of a limited number of electrons have followed this rule approximately.

From the value of the constant k which is determined by the experimental data, it is possible to calculate the radii of the different rings of electrons according to the formula

$$a = \frac{k\lambda}{4\pi(M + \sigma_n)}.$$

Using the values corresponding to the solid curve of Fig. 5 we thus find for the outer ring of calcium, $a = 0.97 \times 10^{-8}$ cm., for carbon, 0.56×10^{-8} cm., and for oxygen, 0.41×10^{-8} cm. The absolute magnitudes here given are of course subject to revision by further experiment, but if the number of electrons in the outer ring is taken equal to the positive valence of the atom, a number of unsatisfactory attempts to obtain expressions for U with other arrangements make it seem necessary that the ratio of the diameters of the rings shall be about that here given. This result is interesting in connection with the fact that while the carbon and oxygen atoms in calcite are only about 1.07×10^{-8} cm. apart, the calcium atom is about 2.95×10^{-8} cm. from its nearest neighbor. In the case of rock-salt, if the valency electron of sodium is in the outer chlorine ring, the radius of the next sodium ring is 0.36×10^{-8} cm., and of the outer chlorine ring is 1.00×10^{-8} cm. If the valency electron remains in the sodium atom, it is, according to our assumptions, 1.86×10^{-8} cm. from the center of the atom, and the chlorine ring is reduced to 0.89×10^{-8} cm. This is a possible arrangement, since the atoms are 2.81×10^{-8} cm. apart. As mentioned above, the diameter of the chlorine ring is probably determined with a fair degree of accuracy. The arrangement of the inner rings is by no means so definitely determined. A number of attempts were made, however, to fit the data for rock-salt assuming only 2 instead of 4 electrons in the inner rings, and this seemingly small change made the curve for U depart too far from the experi-

mental values to be acceptable. Results such as these make it reasonable to suppose that in the case of the lighter elements it may be possible, with a sufficient amount of accurate experimental data, to determine positively the distance of each individual electron from the center of its atom.

Bearing on Theories of Atomic Structure.—While it is difficult by any such "cut and try" method to find the only possible arrangement of the electrons in atoms, it is evident that a study of the intensity of X-ray spectra thus affords an extremely sensitive test of any theory which assigns a definite distribution to the electrons in atoms. From the experimental data now available it may be said, for example, that unless some important factor has been neglected in our formula for X-ray reflection, it seems impossible to account for the rapid diminution of the intensity of the higher orders on any theory, such as Crehore's,[17] which would confine the electrons of an atom within a distance less than 10^{-10} cm. from its center. Such a distribution would make the quantity ψ of equation (6) approximately equal to unity, and this equation would then differ from the experimental equation (1) by the factor $\tan\theta$, which is much greater than the experimental error. Even if such a factor were introduced into the theoretical equation, it would still be unable to account for the variations in intensity which are characteristic of the individual crsytal used as a grating. It seems necessary, therefore, to reject Crehore's theory of the atom as an impossible hypothesis.

On the other hand, it seems possible to explain all the X-ray intensities on the basis of the type of atom suggested by Bohr.[18] The working assumption that we have used, the constancy of angular momentum, is the fundamental hypothesis of Bohr's theory. We may calculate the angular momentum of the electrons in the atoms here considered according to the relation

$$c = \sqrt{k\frac{\lambda m e^2}{4\pi}}.$$

Using the values $\lambda = 0.614 \times 10^{-8}$ cm., $m = 9.0 \times 10^{-28}$ gm. and $e = 4.77 \times 10^{-10}$ gm.$^{1/2}$cm.$^{3/2}$sec.$^{-1}$, for the outer rings of the atoms in calcite $k = 35.0$ and c becomes 1.87×10^{-27} gm. cm.^{2} sec^{-1}. For the inner rings our hypotheses make c half this value. According to Bohr the angular momentum of an electron in an atom is an integral multiple of $h/2\pi$, where h is Planck's constant. Using the value $h = 6.57 \times 10^{-27}$

[17] A. C. Crehore, Phil. Mag., 26, 25 (1913) and elsewhere.

[18] N. Bohr, Phil. Mag., 26, pp. 1, 476, 857 (1913), 27, p. 506 (1914).

gm. cm.^{2} sec.$^{-1}$, we find $c = 2(1 - .10) \cdot h/2\pi$. In the case of rock-salt it is the outer chlorine ring whose diameter is most definitely defined. In this case $k = 9/4 \cdot 38.2$, and $c = 2.93 \times 10^{-27} = 3(1 - .06) \cdot h/2\pi$. It may be only an accident that the angular momentum in these cases works out so nearly in accord with Bohr's hypothesis, but it is at least a most interesting accident. The difference between the coefficients of $h/2\pi$ and integers is probably too great to be due to experimental error in the determination of the radii of the electronic rings, but there are good reasons to believe that there may be forces acting on the electrons which have not been considered, and which would be sufficient to account for the difference.

SUMMARY.

In the first part of this paper an expression is derived for the energy of a beam of X-rays of definite wave-length which is reflected from a crystal. The result is in accord with that previously derived by Darwin, and shows that the intensity of the reflected beam depends not only upon the angle of reflection but also upon the arrangement of the electrons within the atoms of the reflecting crystal.

The form of the equation for the energy in the reflected beam is shown to be independent of the degree of perfection of the crystal and of the length of the wave-trains of which the X-rays consist.

In the latter part of the paper a study is made of the possible distributions of the electrons in atoms which will account for the observed energy in the reflected beam of X-rays. It is shown that there is no possible distribution of the electrons which will lead to Bragg's empirical law for the intensity of reflection; it is found rather that any formula for this intensity must depend not only upon the angle of reflection but also upon the wave-length of the incident rays.

Attention is called to the fact that Bragg's experimental data indicate differences in the reflection from certain crystals which can arise only from differences in the distribution of the electrons in the atoms of which the crystals are composed.

Assuming a number of electrons in each crystal equal to the atomic number, and making certain plausible assumptions concerning the arrangement of these electrons in rings, it is found possible to account in a satisfactory manner for the observed intensities of the X-ray spectra.

Although the particular distributions assigned to the electrons in the atoms of calcite and rock-salt may not be the only ones which will account for the observed intensities of the X-ray spectra, it seems probable that these distributions are not far from correct.

The results of this investigation seem to show conclusively that the

electrons are not concentrated within a very small distance from the center of the atom, as is assumed in Crehore's theory of atomic structure. On the other hand, the conclusions arrived at are in good accord with the theory of the atom due to Bohr.

My thanks are due to Professor H. L. Cooke for his helpful interest in this research.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
June 19, 1916.

AN EFFECT OF LIGHT UPON THE CONTACT POTENTIAL OF SELENIUM AND CUPROUS OXIDE.

BY E. H. KENNARD AND E. O. DIETERICH.

THE increased electrical conductivity of selenium under illumination has been explained in terms of the electron theory by assuming that the light produced an increase in the number of free electrons, and this explanation is strongly supported by observations on the rate of decay of the conductivity, which suggest the recombination of ions according to familiar laws. It occurred to the authors that the increase in the number of electrons ought to result in a change of the contact potential under illumination, because the electrons would tend to diffuse away from the illuminated region and would therefore leave the selenium more positive than before. A search for this effect was accordingly made; the work was interrupted by the departure of one of the authors, but it seems worth reporting as a quick survey of a new field.

METHODS OF OBSERVATION.

Two methods of observation were used. The first was a condenser method for the measurement of quick changes in contact potential. The plate of selenium, which was about 5 cm. square and 0.2 to 0.4 mm. thick, was mounted between a sheet of gauze above and a copper plate below (cf. Fig. 1), the plates being insulated from each other and when

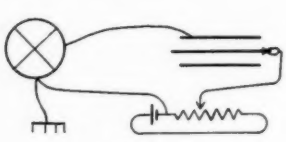

Fig. 1.

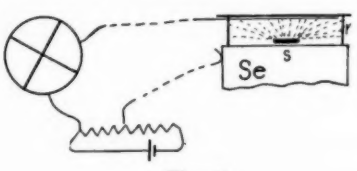

Fig. 2.

desired from earth by means of bits of amber or by supports tipped with sealing-wax. Any one of the three plates could be connected to an electrometer giving 3,000 mm./volt or to an improvised potentiometer, contact with the selenium being made by means of a wire clip; thus any deflection of the electrometer due to a change in the potential of the selenium surface could be nullified by adjusting the potentiometer and the change was thus determined. Readings were usually taken in pairs,

the light being thrown on and then off; the two readings generally differed by 10–20 per cent. but the means of successive pairs agreed mostly within a few per cent.

The second method was an adaptation of the ionization method of measuring contact potentials. An "ion contact" capsule (Fig. 2) was made by coating a copper strip *s* on top with polonium and mounting it in a fiber ring *r* so that it would clear when the ring lay upon a plane surface. The ring was closed on top by a sheet of mica, and just below this was mounted a sheet of brass gauze, one strand of which protruded through the ring and was connected to the electrometer. The mica was of sufficient thickness to stop α-particles and all cracks were closed with soft wax, while the arrangement of the parts prevented α-particles from striking the selenium. The ring was about 12 mm. in diameter and 3 mm. high.

A null method was employed as suggested by Fig. 2. The equalization of potential between gauze and specimen was only about half effected in a minute, corresponding to a resistance of some 10^{13} ohms, but when the sensitiveness of the electrometer was increased to 18,000 mm./volt by the use of a concave lens in front of the scale the adjustment of the potentiometer within a millivolt could be made in less than a minute.

The specimen was illuminated by a 400-watt tungsten lamp placed some 30 cm. away and focused roughly upon it by means of a large lens, a glass dish containing 2 cm. of water being usually interposed to minimize heating effects. Electrostatic screening was carefully attended to, the light being admitted through a sheet of coarse gauze.

Photo-Electromotive Effect in Selenium.

Various connections of the plates in the condenser arrangement were employed, the selenium being connected either to the electrometer or to the potentiometer or left insulated; while the ion contact capsule was used chiefly on a 12-mm. cube of selenium. All the results consistently indicated that illumination suddenly made the surface of the selenium more *negative*, instead of more positive as anticipated. The effect on the plate was usually not far from -0.1 volt, the deflections in the absence of compensation being of the order of 20 mm. Shading the contact on the selenium had no appreciable effect. On the cube mean values of -0.152, -0.176 volt were obtained for a certain face on different days, while later, after washing thoroughly with chloroform, the effect was -0.129 on the same face and -0.125 volt on the opposite face. The latter observations indicate a variation with the state of the surface, which we should rather expect if the phenomenon is a change in the contact potential.

An E.M.F. in a closed circuit containing selenium was looked for repeatedly but without appreciable success. In one case two brass clips were placed on the selenium plate, each touching the plate on one (but not the same) side and insulated from the other surface by a bit of paper. When one clip was now connected to the electrometer and the other to earth, illumination produced a minute deflection that was consistent as to sign but amounted only to .3 mm. (0.1 mv.); the sign was reversed by shading the upper contact. These minute residual deflections may very well be due to a heating effect, for the thermo-electric power of selenium is quite large. It is to be noted however that the actual point of contact between the selenium and the metal was not here appreciably illuminated.

A natural suspicion is that the effect might be due to photo-electric emission from the gauze above the selenium. But aside from the question of quantitative sufficiency, this explanation seems to be ruled out completely by these two facts: first, the effect is sudden and yet no steady current persisted under continuous illumination even when all potentials were kept the same by adjusting the potentiometer; secondly, the effect at once reverses when the light is removed.

The conclusion seems therefore a safe one that the observed effect is due to a sudden change produced by illumination in the contact potential of the selenium surface. In other words, between more and less strongly illuminated selenium there exists what might be called a "photo-electromotive force" tending to drive positive electricity away from the illuminated region.

VARIATION WITH INTENSITY OF THE LIGHT.

The variation of the effect with the intensity of illumination was investigated briefly by varying the voltage on the lamp, using the polonium capsule and the selenium cube. An approximate calibration of the lamp was made in terms of an arbitrary standard.

A high degree of sensitiveness to faint light was at once apparent, for a change in potential of about 3 mv. was produced with only 13 volts on the lamp (normal, 110); the illumination on the selenium must have been only about 0.01 candle-foot. Yet at 25 volts, or 2–3 candle-feet, the effect had increased only to 35 mv. From this point on a series of readings was taken, the light being thrown on and off at 2 min. intervals while its intensity was varied to full value and back. The photo-electromotive potentials are plotted against lamp voltages in Fig. 4, curve *I*, while in Fig. 3 the corresponding mean values are plotted on logarithmic scale against the intensity of the light. Something like an

approach to saturation is evident, for the last light intensity is 2,000 times the first while the photo-electromotive effect is only increased by a factor of 3.6; but the logarithmic curve shows a persistent slow increase proportional to about the fifth or sixth root of the intensity.

Closely similar results were obtained when the light was kept on continuously (except for a short break while changing connections). In this case five minutes was allowed between readings, as a previous test had indicated that a fairly steady equilibrium was thus attained. The results are shown in Fig. 4, curve *II*, the potential of the selenium relative to the gauze in the capsule being plotted against lamp voltage.

Fatigue, Drift and Time Lag.

Curve *I* in Fig. 4 shows clear evidence of fatigue with respect to repetition, for the later readings taken after the lapse of 4–28 minutes are all 2–5 mv. smaller. A similar difference between readings taken in immediate succession was frequently noticed. Fatigue with respect to

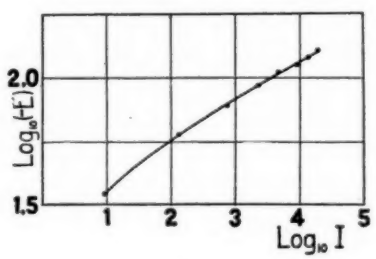

Fig. 3.

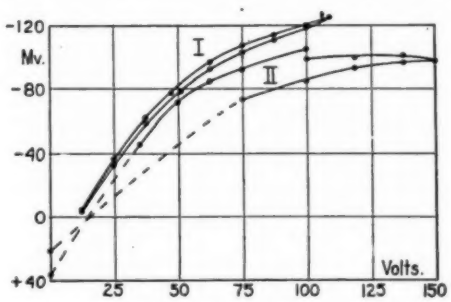

Fig. 4.

continuation, also, is indicated by curve *II*, Fig. 4. The difference in the initial and final dark readings points to a drift of the dark potential toward the negative, yet during the strong illumination the potential was evidently drifting toward the positive: the most natural explanation is that the negative displacement due to illumination tended to decrease with time. Such a drift of the dark potential was frequently noticed; it probably accounted for an apparent hysteresis of 10–20 per cent. that was often observed between the on- and off-readings.

If any time lag occurred when the light was thrown on, it was a matter of seconds only and escaped detection. On the other hand, the change in potential seemed usually to overshoot and then to settle back in the course of several minutes to an equilibrium value.

The Contact Potential of Selenium.

Several comparisons of the contact potential of selenium with that of freshly sandpapered copper were made.

Measurements on two different plates by the usual variable condenser method gave, in the dark, − 0.34, − 0.45 volt, resp. Two faces of the cube were found to be at − .27 and − .36, resp., relative to the gauze in the polonium capsule, while on the same day the latter was observed to be − .099 relative to copper, giving for the selenium − 0.37 and − 0.46, resp. Thus the contact potential of selenium crystallized in mass is not far from − 0.4 volt in the dark relative to freshly sandpapered copper, changing under moderate to intense illumination by about − 0.1 volt.

PHOTO-ELECTROMOTIVE EFFECT IN CUPROUS OXIDE.

Interesting results were obtained on a plate of cuprous oxide, which is also light-sensitive as regards resistance. The plate was about 2.5 cm. square and 1 mm. thick, and was prepared by heating a copper plate at a bright red heat for 48 hours and then dissolving off the surface layer of cupric oxide with aqua regia. The time allowed proved insufficient, however, so that the plate contained a layer of metallic copper down the middle.

The polonium capsule was placed on top of the plate and two clips were attached, one insulated with paper above and the other below. By connecting one clip to the electrometer and the other to the potentiometer it was found that an E.M.F. (voltaic?) of some 20 mv. existed between these two points; under illumination this E.M.F. increased by

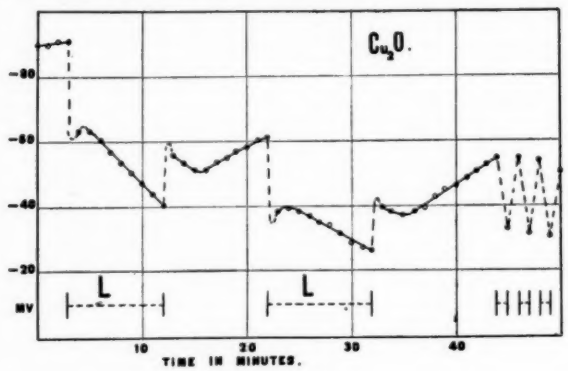

Fig. 5.

7 mv. when the top contact was unshaded but decreased by the same amount when the contact was shaded. When the capsule was connected to the electrometer and one of the clips to the potentiometer, illumination made the surface under the capsule become more positive by 20 to 28 mv.

As in selenium, the initial effect seemed to overshoot and to be followed by a moderate reaction. There was also a decided drift of the potential

in the dark, sometimes in one direction, sometimes in the other, but a true hysteresis was not apparent. A series of readings of the potential at intervals of a minute is shown in Fig. 5, the dotted line marked *L* showing the periods of illumination. Apparently illumination produces, besides the sudden effect, a slow drift of potential followed by recovery in the dark but lagging by 2–3 minutes; this may be a temperature effect. The curve shows decided fatigue with respect to continuation of illumination, the return being practically complete if made at once but amounting to only some 60 per cent. after ten minutes of illumination. Fatigue with respect to repetition does not appear here, but in some of the other readings it was evident to the extent of some 10 per cent.

CONCLUSION.

The negative sign of the effect in selenium disposes at once of the diffusion of electrons as a possible cause. A tempting hypothesis is that the light modifies the molecules in such a way as to diminish the potential energy of the electrons in the intermolecular spaces, and that this results in an increase of the number of free electrons, partly at the expense of the surrounding atoms of selenium and partly at the expense of other bodies with which it is in contact. This would explain both the increased conductivity and the change toward the negative in the contact potential. But the lack of proportionality between the two effects and especially the apparent occurrence of saturation in the latter seem to be fatal objections to this hypothesis. Apparently the two effects are due to independent causes.

The experimental results may be summarized as follows:

1. The contact potential of selenium changes under illumination by an amount exceeding a millivolt for 0.01 candle-foot and tending to show saturation at a value of about -0.1 volt under strong illumination. The phenomenon is complicated by fatigue effects and a slow drift of the potential with time.

2. No E.M.F. is produced however in a closed circuit.

3. The contact potential of selenium relative to freshly sandpapered copper is about -0.4 volt in the dark.

4. The surface potential of a plate of cuprous oxide changed under illumination by about 25 mv.; but the plate also contained a small voltaic (?) E.M.F. which varied under illumination.

The authors take pleasure in acknowledging a debt to Professor A. F. Kovarik for his kindness in preparing the polonium deposit for the ion contact capsule.

UNIVERSITY OF MINNESOTA,
August, 1916.

WAVE-LENGTH ENERGY DISTRIBUTION IN THE CONTINUOUS X-RAY SPECTRUM.

BY BERGEN DAVIS.

PROFESSOR DUANE and F. L. Hunt[1] have described some very interesting and important experiments on the energy radiated at various wave-lengths from a Coolidge X-ray tube.

The Coolidge X-ray tube was operated by a steady high voltage obtained from a large number of small storage cells. This voltage, however, was less than that required to produce the characteristic rays of tungsten. The radiation, after passing through a slit, was reflected from a cleavage surface of a calcite crystal. The wave-length was determined in the usual manner by the angle of reflection and the intensity of the radiation was measured by the ionization produced in the ionization chamber of the spectrometer. In this way an experimental relation was obtained between the energy and the wave-length of the radiation from a Coolidge X-ray tube.

The results of one experiment are shown by the full line in Fig. 3. This curve is reproduced from the curve published by Duane and Hunt. The results have not been corrected for variation of absorption with wave-length nor for the dependence of reflectivity of the crystal upon wave-length.

There is no radiation emitted at a wave-length less than λ_0. The curve rapidly rises to a maximum and then decreases with increasing wave-length. A point of great interest is that the shortest wave-length λ_0 corresponds to that required by the quantum relation.

$$P_0 e = \tfrac{1}{2} m v_0^2 = h\nu_0 = \frac{hc}{\lambda_0}.$$

The significance of these results is to be found in the fact that although the electrons of the cathode stream all have practically the same velocity, the radiation has a wide range of frequencies less than the frequency (ν_0) required by the Planck equation. Also as the voltage applied to the tube is varied the wave-length (λ_0) at which the curve starts is shifted, the curve still retaining the same form. Dr. A. W. Hull[2] has recently

[1] Proc. Amer. Phys. Soc., PHYS. REV., August, 1915.

[2] Proc. Amer. Phys. Soc., PHYS. REV., Jan., 1916.

shown that the wave-length (λ_0) of the end radiation fulfills the condition:

$$P_0 e = h\nu_0 = \frac{hc}{\lambda_0},$$

for all voltages applied to the X-ray tube, at least for all voltages up to 100,000 volts, which was the upper limit of the experiments.

It is proposed here to develop a theory of this continuous or " white " X-ray spectrum.

Two distinct hypotheses will be made as to the origin of the radiation.

A. A PULSE HYPOTHESIS.

The radiation will be considered as consisting of the pulses arising from the accelerations of the electrons of the cathode stream upon their impacts with the atoms of the target.

B. A QUANTUM HYPOTHESIS.

The radiation will be considered as arising from electrons of the atom, excited in some manner by the transfer of energy from the electrons of the cathode stream. The quantity of energy radiated will fulfill the condition:

$$\epsilon = h\nu.$$

The frequency also is controlled by the condition:

$$\tfrac{1}{2}mv^2 = h\nu.$$

In this hypothesis, only a small fraction of the electrons of the cathode stream make impacts that are effective in exciting radiation.

A. THE PULSE HYPOTHESIS.

The following fundamental assumptions are made:

(*a*) The " white " or continuous X-radiation are the electro-magnetic pulses produced by the accelerations of the electrons of the cathode stream upon their collisions with the atoms of the target. (The Stokes pulse theory of X-rays.)

(*b*) The energy radiated by an impinging electron is given by the equation:

$$E = \frac{2}{3}\frac{e^2}{c}\int a^2 dt,$$

where a is the acceleration of the electron, e is the charge and c is the velocity of propagation.

(*c*) The frequency (ν) of the emitted radiation fulfills the condition:

$$\tfrac{1}{2}mv_n^2 = h\nu,$$

where v_n is the component of the velocity of the electron normal to the atomic surface.

(*d*) The atoms of the target are considered to possess centers of force that strongly repel the colliding electrons. The repulsive force varies inversely as the cube of the distance from the center of force, and has a spherical distribution about this center.

(*e*) The electrons do not lose all of their kinetic energy at a single collision, but as they thread their way down through the surface of the target they lose their energy (velocity) by successive collisions with the atoms. These successive collisions continue until the translational energy of the electrons is exhausted.

A distinction is here made as to the nature of the continuous X-radiation and the characteristic radiation. The continuous radiation which is due to the accelerations of the impinging electrons is probably independent of the nature of the atoms of the target, except in so far as the repulsive force of the atoms for the electrons may depend on atomic properties. The characteristic radiation on the other hand depends directly on the atomic number of the element composing the target. This radiation arises from the electrons within the atom while the continuous radiation originates in the accelerations of the electrons of the cathode stream.

The difference between the continuous X-ray spectrum and the characteristic radiation is exhibited in a striking manner by the curves in Fig. 1, which Dr. A. W. Hull, of the Research Laboratory of the General Electric Company, has kindly allowed me to reproduce here. Curve 1 is the spectrum of the radiation from a tungsten target, and curve 2 is that from a molybdenum target. They were both taken at the same voltage of 43,000 volts. This voltage is less than that required to produce the characteristic radiation of tungsten, and is similar to that obtained for tungsten by Duane and Hunt (see Fig. 3). The voltage, however, is greater than that required to produce the characteristic rays of molybdenum. The curve 2 shows the characteristic (line) radiation superimposed on the continuous spectrum. The intensity of the characteristic radiation is great compared to that of the continuous spectrum.

The way in which the characteristic (line) spectrum is added to the continuous indicates that the two radiations may have different origins, and suggests the view advanced here, that the one arises from the electrons of the atoms and the other from the electrons of the cathode stream. These two curves (Fig. 1) were obtained under identical conditions.

When an electron impinges on the atomic surface (region of repulsive force), it is accelerated and a pulse is emitted. In two papers on a

pulse theory of temperature radiation, Sir. J. J. Thomson[1] has described the kind of impact required by the laws of such temperature radiation. For the sake of brevity the results obtained by Professor Thomson will be applied to the present problem.

(*a*) It is shown that in order that the radiation may satisfy the second

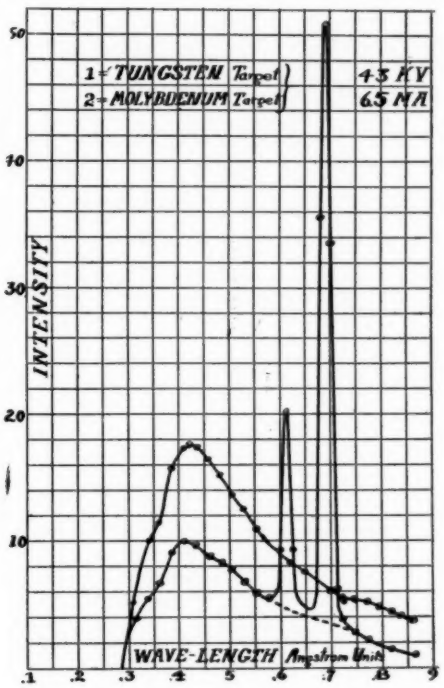

Fig. 1.

law of thermodynamics, the product of the kinetic energy of the colliding electron and the time of impact with the atom must be equal to a constant. This condition may be represented by:

$$\tfrac{1}{2}mv_n^2 t = H = \text{a constant.} \qquad (1)$$

This is similar to Planck's quantum relation since a frequency is a reciprocal of a time.

(*b*) It is shown that the inverse cube law of force between the colliding electron and the atom gives approximately the above relation between the impact time and the kinetic energy of the electron.

(*c*) It is shown that approximately the rate of emission of energy during the impact of an electron is:

$$E = \frac{2}{3}\frac{e^2}{\pi e}\frac{v_n^2}{t}, \qquad (2)$$

[1] Phil. Mag., August, 1907, and July, 1910.

whose v_n is the normal component of velocity at beginning of the collision and t is the duration of the impact.

The radiation (2) may be expressed in terms of the normal velocity v_n by means of equation (1)

$$E = \frac{1}{3}\frac{m}{H}\frac{e^2}{\pi c} v_n^4. \tag{3}$$

The energy is proportional to the fourth power of the normal component of the velocity of the colliding electron.

It is assumed that there is some constant relation between the pulse length and the wave-length at which a greater part of the energy is radiated. That is, the constant H of equation (1) has such a value that the frequency of the radiation approximately fulfills the conditions of the quantum hypothesis:

$$\tfrac{1}{2}mv_n^2 = h\nu.$$

The energy radiated is:

$$E = \frac{4}{3}\frac{e^2}{m}\frac{h^2}{c\pi H}\nu^2.$$

or

$$E = k\nu^2. \tag{4}$$

The *energy radiated* is *proportional* to the *square* of the *frequency*.

B. Quantum Hypothesis.

There are serious objections to a pulse theory of the origin of X-radiation. It is doubtful if any pulse theory can satisfy all the results of experiment.

The diffraction effects obtained by means of the crystal grating indicates interference of many successive waves. There can be no true interference by the reflection of a single pulse from the successive molecular planes of the crystal. The pulse may however be resolved into its harmonic constituents and the interference may occur between the successive waves of each frequency. The crystal may perhaps possess the power of making such analysis of the pulse. But this would not lessen the difficulty. The resolution of a pulse into its harmonic constituents would in general give a series of harmonic terms extending to infinite frequency, whose coefficients might have definite magnitudes. The experiments however show that there is no measureable energy present at a frequency greater than the end frequency ν_0. In order to apply the pulse theory one must assume all the coefficients of the higher terms to be approximately zero. The investigation of Professor Thomson, however, previously referred to, shows that this is not the case.

It is quite possible that the mere acceleration of an electron may not necessarily cause radiation. The pulse hypothesis is of course founded on continuous mechanics. The ability of an electron to emit radiation may be in some way dependent on its position with reference to an atom. The success of the Bohr model of the atom strongly suggests that this may be so.

If a system of discontinuous mechanics is required, then of course a pulse hypothesis of radiation is not possible, and one must adopt some form of quantum theory to account for the radiation.

There are a number of physical phenomena that indicate that exchanges of energy probably take place in "quanta." In addition to temperature radiation one might mention the photo-electric effect, the excitation of characteristic X-radiation by impact of cathode rays, the secondary characteristic X-rays and other phenomena. All of these phenomena apparently involve exchanges of energy in definite quanta.

The following assumptions are made:

(*a*) If the impinging electron excites X-rays at all, it transfers all of its normal kinetic energy (that part of its energy due to the normal component of its velocity) into radiant energy.

(*b*) Only a small fraction of the collisions of the electrons result in the production of radiation. This small fraction of the electrons that is effective in producing radiation may be expressed as the probability p that any one electron makes an effective collision.

(*c*) The probability p that any one electron will produce X-radiation is taken proportional to the kinetic energy due to the normal component of its velocity

$$p = C\tfrac{1}{2}mv_n^2,$$

where C is a constant. Actual experiment of course shows that but a small proportion of the energy of the cathode stream appears as X-radiation. The greater part of the energy appears as heat in the target.

The energy emitted by the effective electron will be

$$\epsilon = h\nu.$$

The probability that any one electron in an encounter with an atom will emit radiation is p. The energy emitted by any one electron at an effective impact will be:

$$E = ph\nu.$$

This probability p is placed proportional to the kinetic energy due to the normal component of the velocity.

From which

$$E = C\tfrac{1}{2}mv_n^2h\nu.$$

But

$$\tfrac{1}{2}mv_n^2 = h\nu.$$

The probable energy emitted by one electron at a collision now becomes:

$$E = Ch^2\nu^2. \tag{5}$$

This expression is of the same form as equation (4).

The energy emitted is proportional to the square of the frequency.

The foregoing derivation of course, does not attempt to explain the process, or state the conditions that must obtain in order that an occasional electron shall be effective in producing radiation.

THE RESULTANT RADIATION FROM THE TARGET.

A general expression for the radiated energy in terms of the frequency having been obtained, it remains to derive an equation for the resultant radiation produced by all of the electrons of the cathode stream upon their collisions with the atoms of the target. The electrons of the cathode stream all have the same original velocity ν_0 upon impact with the atoms at the surface of the target. The velocity at which they collide with the atoms progressively decreases.

All frequencies below the end frequency ν_0 may be emitted by the impact of the electrons against the atomic "surface." The forces acting are considered to be radial forces and hence only the normal component of the velocity will be affected, and this component only will determine the frequency. Thus electrons making impact at the pole p of an atom will emit the highest frequency, while those making impact at an angle will emit a lower frequency corresponding to that component of the velocity which is along the radius. This process will take place for all the impacts taking place with the atoms at various depths within the target. The total radiation at any frequency will be found by summing the radiations emitted at the impacts of the electrons that have a normal velocity component corresponding to that frequency as they make successive collisions with the atoms of the target.

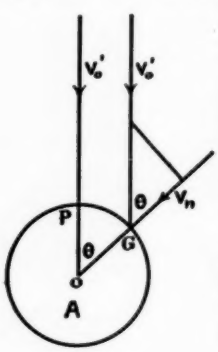

Fig. 2.

Let n' be the number of electrons that impinge on a zonal element of the surface of an atom at an angle (see Fig. 2). The radiation produced by these n' electrons will be by equation (4) or (5).

$$E = kn'\nu^2.$$

The frequency of the radiations may be expressed by:

$$\tfrac{1}{2}mv_n^2 = h\nu. \tag{6}$$

The electrons possess a velocity ν_0 at any depth within the target,

and those that make impact at poles p of the atoms will emit radiation of frequency ν_0'.

$$\tfrac{1}{2}m(v')^2 = h\nu_0'. \tag{7}$$

Since

$$v_n = v_0' \cos\theta,$$

the frequency emitted at any angle θ may be expressed in terms of the polar frequency ν_0'.

$$\nu = \nu_0' \cos^2\theta. \tag{8}$$

If I is the number of electrons that strike the atomic surfaces in an element of time (number of impacts), then

$$n' = I2 \sin\theta \cos\theta d\theta. \tag{9}$$

The energy radiated by all those electrons having a velocity v_0', that make impact on a zonal element of surface of an atom will be

$$dw = kI(\nu_0')^2 \cos^4\theta(2 \sin\theta \cos\theta d\theta).$$

By differentiation of equation (8) and substituting in above

$$dw = -kI\nu_0' \left(\frac{\nu}{\nu_0'}\right)^2 d\nu. \tag{10}$$

This expresses the energy lying between a frequency ν and $\nu + d\nu$ emitted by those electrons having a velocity v_0'.

This velocity v_0' is any velocity at any depth x within the surface of the target.

In order to derive the total radiation it is necessary to express the number of impacts at any velocity at any depth of penetration.

Let v_0 be the velocity with which N electrons enter the surface of the target. The number n_1 found in a layer dx deep will be

$$n_1 = N\frac{dx}{v_0}.$$

The number n present in any layer dx at any depth will be

$$n = n_1 \frac{v_0}{v_0'},$$

where v_0' is the velocity at any depth.

From these two expressions we obtain

$$n = N\frac{dx}{v_0'}.$$

The number of impacts will be proportional to the velocity and to the number having that velocity. The number of impacts in any region dx thick is

$$I = nv_0' = Ndx. \tag{11}$$

It is difficult to formulate an expression for the distribution of velocities of the electrons as they pass down through the surface of the target. One may imagine that the electrons will be differently affected, and that although they all enter the surface with the same velocity, yet at a depth within the surface, after a number of chance collisions there must be a wide range of velocities.

Widdington[1] has investigated the decrease of velocity of electrons on passing through thin films of various thickness. The decrease of velocity observed could be very well represented by:

$$v^4 = v_0^4 - ax.$$

Since $V = 0$ at a thickness corresponding to the range R, this may be written:

$$v^2 = v_0^2 \sqrt{1 - \frac{x}{R}}. \tag{12}$$

But this represents the law of velocity decrease for those few electrons only that passed directly through the film without deviation. The greater part of the entering electrons must have been scattered about, many issuing at various angles and velocities and some of them absorbed in the film itself.

The following consideration will show that Widdington's law cannot represent the velocity distribution completely. In the case of a solid target the electrons all strike the surface at the same velocity v_0. At some depth all of the electrons must have lost all of this initial velocity and have acquired the probability velocity distribution required by Maxwell's law for the temperature of the target. At intermediate depths there must be a gradual transition from the velocity v_0 to the Maxwell distribution. The true expression of the velocity distribution at various depths below the surface would be some equation which would gradually change from a velocity v_0 at the surface ($x = 0$) to an approach to the probability distribution as the depth x became greater and greater. It is manifestly a difficult matter to write such an equation empirically.

I have assumed as an *approximation* for the decrease of velocity for small depths of penetration a modification of Widdington's law of the following form:

$$(v_0')^2 = v_0^2 \left[1 - \left(\frac{x}{R} \right)^a \right]. \tag{13}$$

R is the maximum range of the electrons. The exponent a is a constant whose value may depend on the nature of the target.

[1] Proc. Royal Soc., April, 1912.

From equation (13),

$$\nu_0' = \nu_0 \left[1 - \left(\frac{x}{R}\right)^a \right],$$

$$d\nu_0' = -\nu_0 \frac{a}{R} x^{a-1} dx.$$

By substitution these two give

$$dx = -\frac{R}{a\nu_0} \left(1 - \frac{\nu_0'}{\nu_0}\right)^{\frac{1-a}{a}} d\nu_0'. \qquad (13)$$

By means of equations (11) and (13), equation (10) becomes

$$w = kN\nu^2 d\nu \frac{R}{a\nu_0} \int_{\nu}^{\nu_0} \frac{d\nu_0'}{\nu_0'} \left(1 - \frac{\nu_0'}{\nu_0}\right)^{\frac{1-a}{a}}.$$

The indefinite integral of this cannot be obtained, but by expanding and taking four terms:

$$w = kN\frac{R}{a}\,\nu_0 \left(\frac{\nu}{\nu_0}\right)^2 d\nu \left\{ \log\frac{\nu_0}{\nu} - \frac{1-a}{a}\left[1 - \frac{\nu}{\nu_0}\right] + \frac{(1-a)(1-2a)}{4a^2}\left[1 - \left(\frac{\nu}{\nu_0}\right)^2\right] - \frac{(1-a)(1-2a)(1-3a)}{18a^3}\left[1 - \left(\frac{\nu}{\nu_0}\right)^3\right] + \frac{(1-a)(1-2a)(1-3a)(1-4a)}{96a^4}\left[1 - \left(\frac{\nu}{\nu_0}\right)^4\right] \right\}. \qquad (14)$$

The above expresses the energy, lying between a frequency interval ν and $\nu + d\nu$, radiated by N electrons upon their impact with the target of the X-ray tube. The frequency ν_0 is the end frequency or the highest frequency, and is that emitted by those electrons that make impact at the poles (or normal impact) with the first layer of atoms in the surface of the target.

It is more convenient for comparison with experimental results to express equation (14) in terms of the wave-lengths.

$$w = kN\frac{R}{a}\frac{1}{\lambda_0^3}\left(\frac{\lambda_0}{\lambda}\right)^4 d\lambda \left\{ \log\frac{\lambda}{\lambda_0} - \frac{1-a}{a}\left[1 - \frac{\lambda_0}{\lambda}\right] + \frac{(1-a)(1-2a)}{4a^2}\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^2\right] - \frac{(1-a)(1-2a)(1-3a)}{18a^3}\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^3\right] + \frac{(1-a)(1-2a)(1-3a)(1-4a)}{96a^4}\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^4\right] \right\}, \qquad (15)$$

Equation (15) is compared to the experimental results in Figs. 3, 4 and 5 where the broken line represents the plot of the equation. Fig. 3

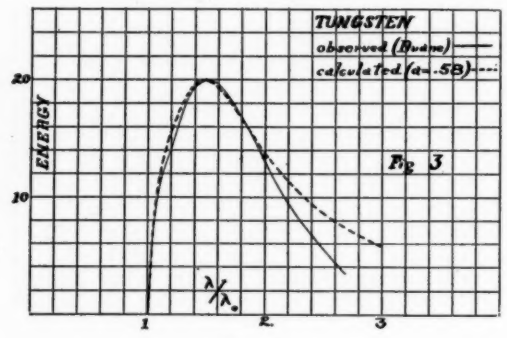

Fig. 3.

(the full line) represents the experimental results obtained by Duane and Hunt for a Coolidge tube with a tungsten target.

Figs. 4 and 5 represent the results for tungsten and molybdenum tar-

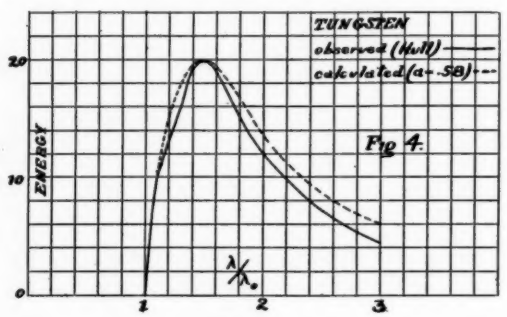

Fig. 4.

gets, kindly furnished me by Dr. A. W. Hull. In all of these curves the abscissæ represent the ratio of any wave-length to the shortest or end wave-length. I believe that none of these curves have been corrected

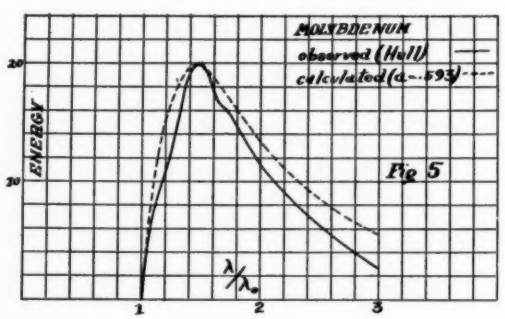

Fig. 5.

for the variation of absorption with the wave-length nor for the dependence of the reflectivity of the crystal upon wave-length.

In calculating equation (15) such a value of a was chosen as would make the maximum of the calculated curve coincide with that of the observed curve. It will be observed in Figs. 1, 4 and 5 that the maximum does not occur at the same ratio of λ/λ_0 for tungsten and molybdenum, but that this ratio is less for the element of smaller atomic number. The constant a also possesses the property of controlling the position of the maximum of the calculated curve. The agreement between theory and experiment is perhaps as good as might be expected, since the assumed law of loss of velocity of the electrons as they penetrate the target can only approximately represent the actual state of the case.

Relation Between the Energy Radiated at Constant Wave-Length and the Voltage Applied to the X-ray Tube.

Professor Duane and F. L. Hunt[1] also investigated the radiation emitted at a *constant wave-length* when the voltage applied to the X-ray tube was varied. The angle of reflection from the crystal was kept constant and the applied voltage was increased by steps. No radiation was observed at voltages less than that given by the relation

$$Pe = h\nu = \frac{hc}{\lambda},$$

but the radiation increases very rapidly with increase of voltage.

The theory here proposed (equations 14 and 15) also expresses a relation between the voltage and the radiation at constant wave-length. The variable in the energy equation in this case is ν_0 while ν remains constant. The constant frequency ν may be expressed by

$$Pe = h\nu,$$

while the variable frequency ν_0 is connected to the variable voltage P_0 by the relation

$$P_0 e = h\nu_0.$$

From these we obtain

$$\frac{\nu}{\nu_0} = \frac{P}{P_0}.$$

If P/P_0 is substituted for ν/ν_0 in equation (14) and for ν_0^2 we write $(e/h)^2 P_0^2$, the equation expresses the energy emitted at constant frequency as a function of the applied voltage. A plot of equation (14) so modified is shown in Fig. 6. The theory indicates that the energy in-

[1] Proc. Amer. Phys. Society, Phys. Rev., August, 1915.

creases rapidly with increasing voltage, but attains a maximum value. This maximum was not observed by Duane and Hunt since their experiments did not extend over a sufficient range of voltage.

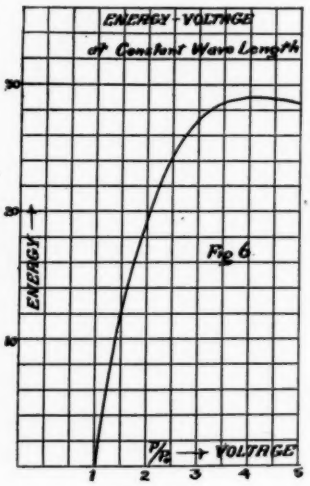

Fig. 6.

The Total Energy Radiated at an Applied Voltage P_0.

The total energy radiated at all wavelengths by an X-ray tube when operated at a voltage P_0 may be found by taking the total area under the curves (Figs. 3, 4, 5). This may be readily accomplished by the integration of equation (14) between the limits $\nu = 0$ and $\nu = \nu_0$.

For a given value of the constant a the terms within the bracket contribute only a numerical constant to the valuation of the integral.

Let J represent this numerical constant.

The integration of (14) gives

$$W = JkN\frac{R}{a}\nu_0^2. \tag{18}$$

Since

$$P_0 e = h\nu_0^2,$$

this becomes

$$W = \frac{k}{h^2}(JNe^2)\frac{R}{a}P_0^2. \tag{19}$$

The total energy radiated in the continuous spectrum (not including the characteristic) is proportional to the *square of the applied voltage.*

This result agrees with the experimental results of Beatty[1] who found that the total energy radiated was proportional to the atomic weight of the target and to the square of the voltage operating the X-ray tube.

In the development on the basis of the quantum hypothesis

$$k = Ch^2.$$

Let the constants JNe^2 be represented by K.

Equation (19) becomes

$$W = KC\frac{R}{a}P_0^2. \tag{20}$$

The range R, that is, the number of collisions of the electrons before losing their energy may be expected to depend on the atomic weight of the element composing the target.

[1] Proc. Roy. Soc., vol. 89, 1913.

Since the constant a varies but little with the atomic weight, one may place a/R proportional to the atomic weight of the target. Also the constant C expresses the probability of an electron making the kind of impact that is effective in producing radiation. This probability may be expected to depend in some way on the atomic weight. It will be assumed that C is proportional to the square of the atomic weight. Equation (20) becomes

$$W_1 = KAP_0^2. \tag{21}$$

where A represents the atomic weight of the element composing the target. This interpretation of the constants brings the theoretical equation in agreement with the results obtained by Beatty for the dependence of the energy upon the atomic weight.

The above result is obtained from the equation developed on the quantum hypothesis. The equation derived on the pulse hypothesis does not contain a natural constant that one may reasonably set proportional to the square of the atomic weight.

I wish to express my acknowledgment to my colleague, Professor A. P. Wills, for valuable assistance and discussion.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY,
November, 1915.

TEMPERATURE COEFFICIENT OF CONTACT POTENTIAL. A REJOINDER.

BY K. T. COMPTON.

PROFESSOR SANFORD has recently published in this journal[1] a criticism of work reported by the writer in an earlier issue.[2]

Professor Sanford first suggests that, in the attempt to measure the contact difference of potential between "the opposing nickel and iron faces, respectively, of two hollow metal boxes," the metal of which the remaining parts of the boxes are constructed would influence the results through the formation of electrolytic cells when the boxes are filled with water. He neglects the fact, however, that the internal resistance of such a cell so far exceeds its external resistance that the resulting potential difference between metal parts of a box is entirely inappreciable. A simple calculation shows that in our apparatus the error introduced would not exceed $4(10)^{-9}$ volt, which is about a million times smaller than the variation in contact difference of potential which we measured.

The second criticism is based on the assumption that we allowed the boxes to remain connected, through tubes, with the water reservoir while making measurements, and that we consequently measured the temperature variation of the electrolytic contact potential. "If this were so it were a grievous fault." I had not thought it necessary to state that both boxes were disconnected from the reservoir while measurements were in progress, and the diagram shows plainly that the earthing connections were made directly to the metal boxes and not to the water reservoir.

Finally, Professor Sanford states that, in deriving Professor Richardson's formula $V_m - V_s = (1/e)(\phi_m - \phi_s) + P$, the constancy of the term $(\phi_m - \phi_s)$ as the temperature varies is *assumed*, contrary to apparently reliable experimental evidence regarding the temperature variation of contact potentials. This is, of course, part of the very theory being tested; but the sufficient constancy of the term $(\phi_m - \phi_s)$ is not assumed, but is a logical consequence, according to the theory, of experi-

[1] PHYS. REV., N. S., 8, p. 95, 1916.
[2] PHYS. REV., N. S., 7, p. 209, 1916.

mental evidence regarding the magnitude of the Thomson coefficient for metals.[1]

It appears, therefore, that Professor Sanford's criticisms are without foundation. The essential similarity of results obtained with different experimental conditions, and direct evidence cited in the writer's original paper, indicate that the discrepancy between theory and experiment is probably due to the presence on the metal of surface films of gas or oxide. To make a valid test it is therefore necessary to devise experimental arrangements to eliminate the films or to extend the theory to include the effect of the films.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

[1] Richardson, "Electron Theory of Matter," p. 452 et seq.

NOTE ON THE DETERMINATION BY JUDGMENT OF THE CONSTANTS OF LINEAR EMPIRICAL FORMULAS.

BY HARRY M. ROESER.

ALTHOUGH physicists are agreed that a true linear variation between two characters is quite uncommon in physical relations, yet there are a great number of cases where a straight line suffices to represent a relation over a limited region well within the errors of observation. In such cases the data may be submitted to computation and the constants of the "most probable" line evaluated by the method of least squares. Such a line is the best that can be had by any means to represent the data. However, many times experimenters feel that on account of the accuracy of the data, or, their implicit faith in their ability to locate a line by eye, that the necessary though rather moderate amount of computation involved in the prim rigor of a least square solution is unjustified. Then the observations are plotted to an appropriate scale and a stretched thread or transparent straightedge shifted about among the points until a position is found that seems to best satisfy the relation between the variables. The "criterion" for location is that the sum of the deviations from the line of the points above should be equal to the sum of the deviations of those below.[1]

In handling the problem according to the latter scheme, evidently a point, fixed in the distribution, through which it be known that the best representative line must pass, and about which the straightedge might be rotated until the best location was found, would be of great practical value. Herein is shown how by a very natural and simple calculation *one* point on the most probable line may be rigorously determined in any assumed linear distribution whatever.

Let $x_1, y_1; x_2, y_2; \cdots x_i, y_i; \cdots x_n, y_n$, be n observations on two quantities x and y which vary according to the relation $y = a + bx$. Let x_m be the mean of the observed values of x, and y_m be the mean of the observed values of y. Then the line that would be given by a least square solution for the constants, a and b, passes through the point $x, y \equiv x_m, y_m$. A proof follows.

[1] Goodwin, Precision of Measurements and Graphical Methods, p. 44.

Consider the "normal equations,"[1] the solution of which give the constants, a and b, by least squares.

$$n \cdot a + b \cdot \Sigma x = \Sigma y. \qquad (A)$$

$$a \cdot \Sigma x + b \cdot \Sigma x^2 = \Sigma xy. \qquad (B)$$

The relation between x and y being $y = a + bx$.

Solve for a in equation (A),

$$a = \frac{\Sigma y}{n} - b \cdot \frac{\Sigma x}{n} = y_m - b \cdot x_m.$$

Substitute this value of a in $y = a + bx$ (the equation of the line to be satisfied),

$$y = y_m - bx_m + bx = y_m + b(x - x_m). \qquad (C)$$

Hence when $x = x_m$, then $y = y_m$, which was to be shown.

This idea admits of generalization to the case where the observations are of different weight. Let $p_1, p_2 \cdots p_n$, be respectively the weights of the above n observations on x and y.

The normal equation (A) then becomes,

$$a \cdot \Sigma p + b \cdot \Sigma px = \Sigma py,$$

whence,

$$a = \frac{\Sigma py}{\Sigma p} - b \cdot \frac{\Sigma px}{\Sigma p},$$

which substituted in $y = a + bx$ gives,

$$y = \frac{\Sigma py}{\Sigma p} + b\left(x - \frac{\Sigma px}{\Sigma p}\right),$$

whence,

$$y = \frac{\Sigma py}{\Sigma p} = y_m', \quad \text{when} \quad x = \frac{\Sigma px}{\Sigma p} = x_m'.$$

In this case x_m' and y_m' are what are termed "general"[2] means of the observed values of x and y respectively.

The point $x, y \equiv x_m, y_m$, or $x, y \equiv x_m', y_m'$, being located near the middle of the range, it serves very advantageously in assisting to locate the line without other arithmetical labor than computing two averages. After the line is located the constants, a and b, are picked from the plot, a being the intercept on the Y-axis and b the slope.

A word of warning is in order here. If, according to the very nature of things, it be known beforehand that regardless of the data the line

[1] It is not considered necessary to enter into any detail concerning the intricate theory of the formation of the normal equations. See any current work on least squares.

[2] See Merriman's, Least Squares, 7th edition, 1913, p. 42, Bartlett, Least Squares, p. 7.

must pass through some known point,[1] x_0, y_0, the above scheme does not give a second point and thus completely determine the line. In this case the known point, x_0, y_0, will be a point in the distribution having infinite weight and consideration of this fact in taking the general mean gives $x_m' \equiv x_0$, $y_m' \equiv y_0$. However should the practical conditions surrounding the experiments be such as to vitiate the absoluteness of the theoretical position of the line, *e. g.*; calibration curves of certain types of instruments having on account of friction more or less indefinite zero error. The point x_0, y_0 loses its weight and is no longer truly an observational value. In cases of this kind the above scheme may properly be applied to locating a point near the middle of the range, the theoretical point, x_0, y_0, being neglected.

The usual " practical " test for location of a line, *i. e.*, that the algebraic sum of the deviations of the observed points from the line should be zero, is satisfied by any line drawn in any direction through the point $x, y \equiv x_m, y_m$, and no line will satisfy the test if it does not pass through this point. As previously carried out, adjusting a line to suit the above conditions amounts to nothing more than an extremely roundabout method of placing a line through the point, x_m, y_m. Knowing beforehand that the line must pass through x_m, y_m invalidates the test completely. This last fact should save much labor to graphical analysts inasmuch as a great deal of the necessity of a " residual " plot is eliminated. See Goodwin, Precision of Measurements and Graphical Methods, p. 60.

U. S. BUREAU OF STANDARDS,
WASHINGTON, D. C.,
September 22, 1916.

[1] As in the case of a uniformly heated rod, $L = L_0 + L_0\beta t$, where L is the length at temperature t and β is the coefficient of expansion. Here the line is obliged to pass through the point $L, t \equiv L_0, 0$, L being the known length at 0°.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE CLEVELAND MEETING.

THE eighty-fourth regular meeting of the Physical Society was held at Nela Research Laboratory, National Lamp Works of the General Electric Co., Nela Park, Cleveland, Ohio, October 27–28, 1916.

There were three sessions for the reading of papers, on Friday afternoon, Saturday morning and Saturday afternoon. President Millikan presided. The following twenty-two papers were presented:

The Precision of Photometric Measurements. F. K. RICHTMYER and E. C. CRITTENDEN.

The Emissive Powers of Tungsten for Short Wave-Lengths. E. O. HULBURT.

On Photoelectric Photometry. JACOB KUNZ.

The Reflecting Power of Tungsten in the Infra-red at Incandescent Temperatures. W. WENIGER and A. H. PFUND.

Note on a Comparison of High Temperature Scales. W. E. FORSYTHE. (By title.)

An Attempt to Detect a Change in the Emissive Properties of Platinum and of Tungsten with a Change in the Method of Heating. A. G. WORTHING.

Photo-electric Potentials in the Schumann Region of the Spectrum. P. E. SABINE.

Electro-chemical Analogies of Photo-chemistry. W. R. MOTT.

Scales for Calculating Watts-per-Candlepower and Candle Power for Tungsten Lamps. HERBERT BELL.

An Ionization Manometer for High Vacuum Measurements. O. E. BUCKLEY.

So-called Ionization Pressure of the Corona Discharge. H. D. ARNOLD.

Experiments on the Production of Metallic Spectra by Cathode Luminescence. ARTHUR S. KING and EDNA CARTER.

The Crystal Structure of Iron. ALBERT W. HULL.

Spontaneous Generation of Heat in Recently Hardened Steel, II. C. F. BRUSH.

Unipolar Induction and the Electron Theory. GEORGE B. PEGRAM.

The Structure of the Surfaces of Liquids and a New Theory of Surface Tension. IRVING LANGMUIR.

A New Thermometer Scale. ALEXANDER MCADIE. (By title.)

Improved Forms of Mercury Vapor Vacuum Pumps: The Condensation Pump. IRVING LANGMUIR.

The Spectra of the B-rays of Radium D E and of Radium and its Products, Determined by the Statistical Method. ALOIS F. KOVARIK and L. W. MCKEEHAN.

The Dielectric Constant of Aqueous Solutions. E. A. HARRINGTON.

An Investigation of the Relative Sensibility of the Average Eye to Light of Different Colors, and some Practical Applications to Radiation Problems. W. W. COBLENTZ and W. B. EMERSON.

Transformation Equations of Tolman and the Photoelectric Effect. JACOB KUNZ.

At a short business session the following resolution was presented by the Council and on motion, adopted.

"WHEREAS, The Natural Academy of Science at the request of the President of the United States has organized the National Research Council for the purpose of bringing into cooperation existing governmental educational, industrial and other research agencies, with the object of encouraging the investigation of natural phenomena, the increased use of scientific research in the development of American industries, the employment of scientific methods in strengthening the national defense and such other applications of science as will promote the national security and welfare, and

"WHEREAS, The American Physical Society is itself organized to promote research in that subject whose methods and results lie at the bottom of well nigh all industries and all sciences.

"*Therefore be it resolved* that the American Physical Society pledge its active and full and continuous support to the National Research Council, and express its readiness to cooperate with it to the largest possible extent in accomplishing the purposes sought in its appointment."

The registration for the meeting numbered forty-five. Visiting members were the guests of the General Electric Company for lunch on both days of the meeting, and also at a dinner given at the Mayfield Country Club Friday evening. At the dinner an opportunity was given members of the society to meet a number of prominent manufacturers of Cleveland, whose business involves important applications of physical principles. For the success of this and other special features of the meeting the society is much indebted to Director Hyde of the Nela Research Laboratory and to members of his staff.

A. D. COLE,
Secretary.

THE CRYSTAL STRUCTURE OF IRON.[1]

BY A. W. HULL.

IN the X-ray analysis of iron a special procedure is necessary on account of the difficulty of obtaining large crystals. The analysis was made in

[1] Abstract of a paper presented at the Cleveland Meeting of the Physical Society, October 27, 28, 1916.

two parts. First, a sample of silicon steel, containing about 3.5 per cent. Si and practically no carbon, was analyzed. This has the advantage over pure iron that the crystals, formed by long annealing at high temp., are so hard that they can be split along cleavage planes without being distorted. Single crystals about 6 mm. square, and 2 mm. thick were isolated and mounted so that a narrow beam from a tungsten target passed through the crystal nearly parallel to one of its principal planes. As the crystal was slowly rotated several complete spectra, formed by this plane and others in the same zone, were spread out on the photographic plate as long straight traces. The angles between these traces give the indices of the respective planes, and the position of the K lines on each trace the spacing of the plane. By rotating about different axes the same plane could be observed in different zones, and its identity and spacing checked. The values obtained are given in Table I.

TABLE I.

Indices of Plane.	Spacing. A. U.
100	1.43
110	2.02
111	.82
211	1.15
310	.90
321	.75

The value of $d_{100} = 1.43 \times 10^{-8}$ cm. requires two atoms for a cube of side $2d_{100}$. A lattice having atoms at cube corners and cube centers satisfies this condition, and gives the observed spacing for the other planes.

Pure iron was then investigated in the form of very fine powder, obtained by reduction of the oxide with hydrogen. A narrow beam of rays from a tungsten target passed through the powder and formed on the photographic plate a kind of generalized Laue photograph, in which every possible plane in the crystal structure had an equal opportunity of reflecting, and reflected all wave-lengths present. What was actually observed was the position of the K lines, which, with the tube running at 110,000 volts, stood out very clearly on the continuous background. The reflection of these lines in different planes appeared on the plate as concentric, nearly circular, lines, whose distance from the center should be inversely proportional, approximately, to the spacing of the planes. The distance of these lines from the center can be measured and compared with the values calculated for the assumed crystal structure. If the assumed structure is correct, every calculated line must be present, and no more, and the intensity must fall off in the manner predicted.

The observed and calculated values are given in Table II. In the calculation it was first assumed that the atoms were arranged on a centered cubic lattice, and that the scattering electrons in each atom were concentrated at its center. The spacings calculated on this assumption are given in column 3, and the intensities in column 5, under A. They agree remarkably well with the observed values, but fail to account for three facts, viz.: (1) That the

TABLE II.

Indices of Plane.	Distance of Line from Center.		Intensity of Line.			
	Obs.	Calc.	Obs.[1]	Calc.		
				A.	*B.*	*C.*
110	.703	.71	1.00	1.00	1.00	1.00
100	1.00	1.00	.46	1.00	.60	.54
211	1.23	1.22	.54	1.00	.60	.46
110(2)	1.42	1.41	.24	1.00	.60	.39
310	1.59	1.58	.18	1.00	.40	.13
111	1.74	1.73	.16	1.00	.60	.29
321	1.89	1.87	.22	1.00	.60	.24
100(2)	——	2.00	——	1.00	.20	.0003
411						
110(3)	2.15	2.12	.12	2.00	1.40	.41
210	2.26	2.24	.03	1.00	.60	.12
332	2.38	2.35	.02	1.00	.60	.15
211(2)	2.50	2.45	.02	1.00	.60	.11
431						
510	2.58	2.55	.10	2.00	1.40	.27
521	2.74	2.74	.02	1.00	.60	.04

intensity of the lines falls off continuously with increasing distance from the center. (2) That the first order 100 reflection is much too weak for its position. (3) That the second order 100 reflection is entirely lacking.

It is very difficult to conceive of any arrangement of point atoms which will satisfy these conditions and still give all the observed lines. We are forced, I think, to look for the explanation in the internal structure of the atoms. If it is assumed that eight of the 26 electrons in each atom are arranged along the cube diagonals at a distance from the center equal to one-fourth the distance to the nearest atom, calculation gives the values of intensity shown in column 6 under *B*. It is seen that condition (2) above is satisfied, and (3) is nearly accounted for, but not (1). If all the electrons are displaced from the center of the atom along the cube diagonals in 4 groups of 2, 8, 8, 8, at distances 1/32, 1/16, 1/8 and 1/4, respectively, of the distance to the nearest atom, all the observed facts are accounted for within the limit of experimental error (*C*, column 7).

This is obviously only a rough approximation to the correct position of the electrons in the atom, and more accurate data will enable us to place them more exactly. The excellent agreement with experiment, however, indicates that it is a step in the right direction, and gives promise that we shall be able, by this method, to determine the positions of all the electrons in the atom.

It may be noted that the above arrangement of electrons and atoms gives to iron the correct valence, corresponding to its position in the periodic table, and suggests a very interesting mechanism for ferromagnetism.

[1] The intensity of the first seven lines was measured with a photometer. The rest were estimated.

The calculation of intensities is based upon four assumptions, which can only be briefly stated here. It is assumed: (1) That the rays, by the time they reach the crystal, consist of long trains of waves, to which the electromagnetic theory is applicable; (2) that the scattering is due entirely to the electrons in the atoms, each of which scatters independently and equally; (3) that the number of electrons in an atom is equal to its atomic number; (4) that the electrons have fixed positions in the atom, about which they move in very small orbits.

A full discussion of these assumptions, and of the experimental data, will be published shortly in the PHYSICAL REVIEW.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

AN INVESTIGATION OF THE RELATIVE SENSIBILITY OF THE AVERAGE EYE TO LIGHT OF DIFFERENT COLORS, AND SOME PRACTICAL APPLICATIONS TO RADIATION PROBLEMS.[1]

BY W. W. COBLENTZ AND W. B. EMERSON.

IN the present investigation the methods are practically the same as used by previous experimenters. In the visual measurements, the spectral light was compared with a standard white light by means of a flicker photometer, and also an equality of brightness photometer. The source of white light was a standardized vacuum tungsten lamp. A cylindrical acetylene flame was used as a source of spectral light. The distribution of energy in the spectrum of the acetylene flame was determined with great care in view of the fact that the disagreements in previous work seemed to be due, in part, to uncertainties in radiometrically evaluating the light stimulus.

Sensibility curves were obtained on 130 persons, of which number 5 were color-blind. The visibility curve of the average normal eye, using 125 observers is wider than previously observed. These data are given in Table I., using a flicker photometer. Only a few observers were able to make accurate settings with the equality of brightness photometer.

As was to be expected the visibility curves of no two persons appear to be exactly alike. When a visibility curve does not coincide with the average there is usually a marked departure from the average visibility in a given spectral region. This gives rise to (1) wide visibility curves with the maximum shifted toward the red, *i. e.*, "red sensitive," (2) narrow curves with a sharp maximum in the green and (3) curves with the maximum shifted toward the violet.

The data available indicate that 60 per cent. of the cases examined fall into three quite evenly divided groups (*i. e.*, 20 per cent., roughly estimated

[1] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27, 28, 1916.

TABLE I.

Average Visibility Curve for Even Wave-Lengths, 125 Observers.

Wave Length.	Visibility.	Wave Length.	Visibility.	Wave Length.	Visibility.
0.400μ	0.010	0.520μ	0.710	0.640μ	0.194
0.410	0.017	0.530	0.862	0.650	0.116
0.420	0.024	0.540	0.954	0.660	0.0670
0.430	0.029	0.550	0.994	0.670	0.0360
0.440	0.033	0.560	0.998	0.680	0.0194
0.450	0.041	0.570	0.968	0.690	0.0095
0.460	0.056	0.580	0.898	0.700	0.0047
0.470	0.083	0.590	0.800	0.710	0.0024
0.480	0.125	0.600	0.687	0.720	0.0012
0.490	0.194	0.610	0.557	0.730	0.0007
0.500	0.316	0.620	0.427	0.740	0.0004
0.510	0.503	0.630	0.302	0.750	0.0003

in each group) which are either (1) red sensitive (2) blue sensitive or (3) average. Similarly 30 per cent. of the cases examined are quite evenly divided into three groups which fall below the average sensibility in either (1) the red or (2) in the blue or (3) in both the red and the blue, thus giving rise to an apparently high sensitivity in the green. One person in 20 has a very wide visibility curve; while 4 per cent. are color blind, *i. e.*, they confuse colors.

The point of maximum sensibility is very different for different observers, and for the 125 persons the maximum is at $\lambda_m = 0.5576\mu$. The curve of average visibility, when corrected for selective transmission of the ocular media, including the yellow spot, is very symmetrical.

The complete paper gives an empirical equation of the visibility curve determined. Using this visibility equation and Planck's equation of black body radiation, calculations are given of the luminous energy emitted by a black body at various temperatures, also the luminous efficiency, the Crova wave-length and the mechanical equivalent of light. Using the recent measurements of the brightness of a black body as determined by Hyde, Cady and Forsythe and the most probable values of the radiation constants ($C_2 = 14{,}350$, $\sigma = 5.7 \times 10^{-12}$) the value is 1 lumen = .00161 watt of luminous flux; or 1 watt (of radiation of maximum visibility) = 621 lumens = 49.5 candles. The direct determination of 613.6 lumens for green mercury radiation, $\lambda = .5461\mu$ (made by Ives, Coblentz and Kingsbury, using 61 observers) when corrected for visibility V (at $\lambda = .5461\mu$) = .985 V_m, gives 622.8 lumens per watt, which is in good agreement with the present determination.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
October 16, 1916.

ELECTROCHEMICAL ANALOGIES OF PHOTOCHEMISTRY.[1]

BY WILLIAM ROY MOTT.

HYDRAULIC and mechanical analogies of electrical and magnetic action are well known to be very useful to physicists and electrical engineers.[2] It is my firm belief that likewise very useful analogies can be shown to exist between electro-chemistry and photochemistry. In line with this, Prof. Bancroft wrote in 1908 an interesting paper, entitled "Electrochemistry of Light"[3] in which the theory of Grotthus was revived. The Grotthus theory of the electrochemistry of photochemistry is rather general and is fairly consistent with our modern electron theory of matter and the electromagnetic nature of light.[4] However, the value of a theory is measured by its power of prediction and in this respect Grotthus's theory has not accomplished much.

As a result of my experiments on dye fading and other photochemical reactions,[5] I have come to the conclusion that the general theory of the electrochemistry of photochemistry can be revised to a more concrete form in which the two electrochemical factors of current and voltage are respectively related to amount of light and wave-length of light.

Electrochemical Analogy of Current and Amount of Light.—The first law of photochemistry is that the amount of chemical action is nearly proportional to the energy of the light absorbed in the photochemical reaction chamber. The first law of electrochemistry is that the amount of electrolysis is proportional to the current passed through the electrochemical cell. (This law in its complete form with reference to electrochemical equivalents, is known as Faraday's law of electrolysis.) (The law of photochemistry is generally known as Draper's law although Grotthus also proposed it.) The amount of photolysis is proportional to absorbed energy provided the wave-length of light is of a short enough value. This is anticipating our next section, however, but the same limitation exists as regards Faraday's law of electrolysis where sufficient voltage must be supplied to exceed the decomposition voltage of the material being electrolyzed. Further decrease in wave-length or increase in the voltage of a cell does not affect respectively the proportion of photolysis or of electrolysis. The physicist Lasareff[6] showed that dye fading in respect to spectral distribution depends on amount of absorbed light energy. He says "Within the limits of experimental error, the amount of dye stuff which is destroyed (by the light) is directly proportional to the amount of absorbed

[1] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27, 28, 1916.

[2] See book on Electricity and Magnetism, by W. S. Franklin and B. MacNutt.

[3] See Am. Electrochem. Soc., 13, p. 244.

[4] See Henri Compt. rend., vol. 156, p. 1979.

[5] See "Use of Flame Arc in Paint and Dye Testing Trans. Am. Electrochem. Soc. vol. 28, p. 371 1915; also "The Flame Arc in Chemical Manufacture," C. W. Bedford and writer, Jour. of Ind. & Eng. Chem., vol. 8, p. 1029, 1916.

[6] Ann. der Physik, 1907, 24, p. 661.

energy and is independent of the wave-length of the incident ray in an absorption band (of the dye solution)." Also V. Henri and R. Wurmser[1] found that there is a striking similarity between the absorption curve for acetone in ultraviolet and the chemical activity of the different rays. Hence there is shown a working analogy between current in electrolysis and light energy absorbed in photolysis.

The great importance of absorbing media in photochemistry leaves no apparent relation to electrochemical equivalents as in electrochemistry in going from one material to a different material. This is the natural limitation of the analogy. However, with a given material under photolysis the departure from apparent proportionality to amount of absorbed light energy can be explained in general in a way parallel to apparent departures of electrochemical reaction in a given electrolyte from Faraday's law. For instance, at a current of one millionth of an ampere per square centimeter experiments by Dr. H. E. Patton and the writer in 1903 showed extremely little electrochemical polarization,—due to what is electrochemically known as residual currents. In the same way in photochemistry, there is a limiting low exposure beyond which no apparent record of photolysis is obtained.[2] As the coulombs or the candle power meter seconds exposure are increased, a marked similarity of phenomena can be noted. The region of residual current is generally due to a secondary reaction calling for extremely little energy and according to the law of least work, the easy reaction takes place before the reaction calling for more energy. A marked case of this kind with electrolytic cells is obtained by mixing certain oxidizing and reducing agents—for example ferrous and ferric salts and then large residual currents can be readily passed with little or no polarization—although no doubt chemical analysis at each electrode would show Faraday's law to have been obeyed. This brings us then to the voltage factor of electrolysis versus the intensity factor in photolysis.

Electrochemical Analogy of Voltage and Wave-length.—The intensity factor or voltage analogy is found in light in increased frequency (shorter wave-lengths giving greater energy intensity). As a rule, the shorter wave-lengths can decompose the more stable compounds (not decomposed by longer wave-lengths) calling for a higher decomposition voltage electrochemically. It is well known that infra-red rays are extremely lacking in power to cause chemical change whereas ultraviolet rays affect chemically an enormous number of substances. In photoelectric currents, much physical work has shown that certain limiting longer wave-lengths were not effective. The curves of these effects with reference to wave-length of light are quite similar to decomposition curves in which the critical wave-length would hold analogous place to voltage of decomposition.

Berthelot and Gaudechon[3] have shown that high frequency of vibration of light plays the same rôle as high temperatures in heat reaction. I extend this

[1] Compt. rend., 1912, 155, 503.

[2] See P. Villard, J. Physique, 4, 6, 369–79, 445–57, 1907.

[3] Compt. rend., 156, p. 889, p. 1243, 1913.

to say that high frequency of vibration of light plays the same rôle as high decomposition voltages in electrolysis. For instance the halogen compounds illustrate very well the analogy, the fluorides being most stable and resisting light to a marked degree. For example silver fluoride is said to be not sensitive to light. The bromides are more easily decomposed than the chlorides or fluorides, consistent with their decreased voltage of decomposition. The following table illustrates the generalization.

Material.	Formula.	Voltage for Dec.[1]	
Calcium fluoride.....	CaF_2	4.7	Most transparent to far ultraviolet.
Hydrofluoric acid.....	HF	2.2	Not decomposed by far ultraviolet.
Hydrochloric acid.....	HCl	1.7	Slightly decomposed by far ultraviolet.
Hydrobromic acid.....	HBr	1.2	Easily decomposed by ultraviolet.
Hydriodic acid.....	HI	.6	Easily decomposed by blue light.

A curve could probably be constructed between wave length of light required and decomposition voltage required. It is interesting to note that the extremely short waves are readily absorbed by everything except the *non-reactive* noble gases.

This theory can be further expanded to show a relationship between heat of formation (on electrochemical equivalents) and refractive index and point of probable absorption of light as the curve is carried into ultraviolet region. Also, the theory has fascinating possibilities in predicting the character and probability of light production by chemical change.

RESEARCH LABORATORY,
NATIONAL CARBON COMPANY,
CLEVELAND OHIO.

A NEW THERMOMETER SCALE.[2]

BY ALEXANDER MCADIE.

IN a previous communication[3] the writer urged the importance of adopting scientific units in aerophysics. At Blue Hill Observatory, summaries of air pressure and vapor pressure are published in kilobars or force units, temperature in degrees Absolute centigrade; and wind velocities in meters per second. The latest publication of the British Meteorological Office, the Réseau Mondial, gives world data for 1911 in similar units, a noteworthy advance. Passing for the present, the true conception of a megadyne atmosphere and the proper definition of the *bar* as a basic unit, representing the

[1] Calculated from thermal data and actual electrolysis of solutions of halogen acids. See writer's paper, Am. Electrochem. Soc., V., p. 85, 1904.

[2] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27, 28, 1916.

[3] PHYSICAL REVIEW, Vol. VI., No. 6, Dec., 1915.

force which would impart to a gram, an acceleration of one centimeter per second; and not the multiple erroneously used by Bjerknes and other European meteorologists, we may ask, at this stage whether the Absolute scale is best adapted to the needs of meteorologists and climatologists. Physicists will generally concede that the Fahrenheit scale has outlived its usefulness. Many meteorologists however have opposed the introduction of the Centigrade scale (and therefore the Absolute) on the ground that even when read to tenths, the scale division of the latter was too large for meteorological purposes. To meet this objection the writer suggests a new scale to be known as the New Absolute or briefly New. The zero of the new scale will be the same as that of the absolute, approximately 491 degrees below freezing on the Fahrenheit and 273 degrees below on the Centigrade. The other fiducial point is the temperature of melting ice at a pressure of 1,000 kilobars and is marked 1000°. Thus the scale divisions .366° of a Centigrade degree are even smaller than the Fahrenheit and permit of the refinement of reading desired by meteorologists. The new scale has other advantages.

First, the abolition of minus signs. In all upper air work temperatures are as a rule far below freezing. At a height of 10 kilometers we have to deal with temperatures as low or lower than those experienced by Scott in the Antarctic. For example, − 66.0° F., − 54.0° C. or 218.4° A. is on the New scale 800; or if we take some of the winter surface temperatures of our own cities (Cleveland for instance) we have − 17.5° F., − 27.0° C. or 245.7° A. represented by the reading 900.

Second, the great distinction between *warm* and *cold* as experienced in the every-day affairs of life is plainly marked; thus temperatures below freezing are below the 1000° mark; and temperatures above so-called summer heat are above 1100°.

Third, there is a saving of figures and increase of accuracy in tabulation and computation. The weather bureau insists on readings to the tenth of a degree. A reading, − 10.8° F. requires seven pieces of type if printed. The equivalent temperature on the new scale is 915 N. (four pieces).

Fourth, the arrangement of the new scale makes for clearer conceptions of the magnitude of temperature changes. It is astonishing how vague are the conceptions of temperature held not only by the public in general but by those trained in universities and even technical schools. And I may be pardoned for quoting here even before a body of physicists from Professor Ames's little book, "The Constitution of Matter": "There is no word in our language, I think, which is so much used to conceal ignorance as 'heat' and no word about which there is so much confusion of ideas as 'temperature.' "

Finally in thermodynamic problems and also problems of radiation, the New scale would seem to be serviceable, starting as it does from the temperature of no molecular motion and laying emphasis as it does on the one great physical change of state of water, familiar to all.

BLUE HILL OBSERVATORY,
HARVARD UNIVERSITY.

SO-CALLED "IONIZATION" PRESSURE OF THE CORONA DISCHARGE.[1]

BY H. D. ARNOLD.

IN articles by S. P. Farwell,[2] J. Kunz[3] and E. H. Warner,[4] data has been given on the sudden increase in pressure that results when a corona discharge takes place in a closed chamber. Prof. Kunz has developed a theory of the phenomenon assuming the pressure increase to be due to the presence of extra particles produced by ionization. Results by Warner appear to confirm Kunz's theory in that they show the pressure increase to be proportional to the corona current.

If, however, we compute the corona currents that would result from the presence of enough ionized particles to produce the observed pressure changes, the currents calculated are many thousand times greater than those actually obtained. It appears probable therefore that some cause other than ionization contributes largely to the pressure increases which are observed.

In his theory Professor Kunz neglects the thermal expansion which must result from the dissipation within the tube of the power represented by the product of the corona current and the corona voltage. Simple calculations show that the pressures thus generated are of the same magnitude as those observed and that the pressure effects will appear quite suddenly when the corona discharge starts. Experimental verification of this is obtained by electrically heating the central wire in apparatus similar to Farwell's and observing the resulting pressure increase.

When the same power is dissipated in the wire as was used in Farwell's corona discharge the pressure increase observed is somewhat larger than that shown in Farwell's data. This would be expected, for in the corona the power loss is distributed throughout a considerable volume and hence the heat generated can be removed with less temperature (and therefore, pressure) rise than is the case with the hot wire. The agreement between the results is however, such as to show that the magnitude and suddennesss of the so-called "Ionization Pressure" can be entirely accounted for by thermal expansion of the gas.

NEW YORK CITY.

PHOTO-ELECTRIC POTENTIALS IN THE SCHUMANN REGION OF THE SPECTRUM.[1]

BY P. E. SABINE.

THIS is a preliminary report of work done at the Jefferson Physical Laboratory. A monochromatic illuminator, a modification of Lyman's

[1] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27, 28, 1916.

[2] Proc. A. I. E. E., November, 1914, p. 1631.

[3] PHYS. REV., July, 1916, p. 28.

[4] PHYS. REV., September, 1916, p. 285.

vacuum spectrometer, has been made and calibrated for wave-lengths between 230$\mu\mu$, and 125$\mu\mu$. The maximum potentials acquired by a zinc plate under the action of light of wave-lengths, between 185$\mu\mu$, and 125$\mu\mu$ have been measured. The surfaces had been prepared in air. The voltage-frequency relationship was found to be quite independent of the surface condition of the metal when precautions were taken to insure the constancy of these conditions while the measurements for the different wave-lengths were being made. The voltage-frequency relation was found to be strictly linear, but the slope of the line proved to be only 60 per cent. of that called for by the Einstein equation. Following Millikan's suggestion that the small slope obtained by earlier experimenters could be accounted for by the effect of stray light of short wave-lengths, the magnitude of this effect was investigated. With the monochromator set for wave-length 185$\mu\mu$, and a source of light in which the longest wave-length was 167$\mu\mu$, a decided photo-electric leak was observed. The voltage-current curve for this stray light effect was found to coincide very closely with that due to the strongest group of lines in the source. The stray-light effect would accordingly account for the small slope in this and probably in all other experiments in which it is not eliminated by the use of color screens. Such screens for use in the Schumann region of the spectrum have not yet been obtained.

The measurements for $\lambda 125\mu\mu$, the limit of the transparency of fluorite, were not subject to this source of error. Consequently measurements of the maximum potential attained by plates of zinc, cadmium, and copper under the action of this wave-length were made. Contact potential measurements were made simultaneously. The mean value for zinc was 6.70 volts, for cadmium 6.57 volts, and for copper 6.68 volts. These values for zinc and cadmium, taken with the earlier measurements of Hughes, corrected for contact potential difference, give values of h in the Einstein formula of 6.58×10^{-27} $\frac{\text{ergs}}{\text{frequency}}$ and 6.71×10^{-27} $\frac{\text{ergs}}{\text{frequency}}$ respectively. The value of 6.68 volts for $\lambda 125\mu\mu$ in the case of copper is not in agreement with the very low value of the slope of the voltage-frequency line for this metal reported by Richardson and Compton.

CASE SCHOOL OF APPLIED SCIENCE,
CLEVELAND, OHIO.

EXPERIMENTS ON THE PRODUCTION OF METALLIC SPECTRA BY CATHODO-LUMINESCENCE.[1]

BY ARTHUR S. KING AND EDNA CARTER.

AN apparatus has been constructed in which a substance whose spectrum is to be examined may be vaporized through the heat generated by a pencil of cathode rays. These are concentrated upon it by a concave cathode,

[1] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27, 28, 1916.

the anode being so placed as to keep the conduction current away from the anti-cathode. The whole is enclosed in a bell-jar which may be pumped out to a high vacuum.

In the preliminary experiments thus far carried out, the spectra of calcium and iron have been examined in this way, the luminescent vapor in the stream of cathode rays a short distance above the anti-cathode being examined. An electro-luminescence is thus obtained, away from direct heating effects and from the conduction current.

Twenty-six lines of calcium and forty-two lines of iron were photographed. The calcium list includes most of the stronger lines from λ3100 to λ5100 and shows what may be expected from a discharge of this kind. The spectrum resembles that of the arc more nearly than any other of the usual sources, but is distinctive in the relative intensities of the lines. Thus λ4227 is very strong, as in the furnace and flame, but also remarkably sharp. Two series of single lines, to which class λ4227 probably belongs, are much strengthened. Two pairs of lines which are enhanced in the spark spectrum are also strong here, while the series of triplets are relatively weak. The general feature of this discharge, as was also noted by Lewis in his experiments on cathodo-luminescence of metals, appears to be an ability to bring out the more fundamental vibrations. According to this view, the series of single lines, of pairs, and of triplets are of increasing complexity in their vibrations and are arranged in this order in the facility with which they are given by the cathode excitation.

The iron lines thus far photographed are relatively few compared with the richness of this spectrum and are the lines most easily brought out in flame, furnace, arc, and spark spectra. The enhanced lines of the spark and those relatively weak in the arc but strong in the furnace did not appear.

The nitrogen spectrum, consisting of both positive and negative pole bands, was given by the residue of air in the chamber. The negative pole bands were much the stronger, which is in harmony with the view that these are excited by cathode rays.

MT. WILSON SOLAR OBSERVATORY,
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THE PRECISION OF PHOTOMETRIC MEASUREMENTS.[1]

BY F. K. RICHTMYER AND E. C. CRITTENDEN.

PROGRESS in any department of physical science, as was pointed out by Professor Zeleny, is dependent in large measure upon our ability to make more and more precise measurements. It is of interest, therefore, to inquire into the present available precision in the various lines of experimental work in order to determine what factors make greater precision possible. The present paper is the result of an analysis of 20,000 observations showing the precision attainable in a number of different kinds of photometric measure-

[1] Abstract of a paper presented at the Cleveland meeting of the Physical Society, October 27–28, 1916.

ments: with a Lummer-Brodhun photometer for both a color match and a color difference; also with the flicker photometer for a large range of color differences. The precision attainable with the Lummer-Brodhun was approximately 0.3 per cent. for color match; increasing color difference caused a marked decrease in sensibility. With the flicker photometer the precision 0.75 per cent., approximately independent of color difference, was obtained. By precision is here meant average deviation of a single observation from the mean of its set.

NOTE ON THE AMOUNT OF ERROR IN APPLYING TO NON-PARALLEL PLATES THE FORMULA FOR ELECTRICAL CAPACITY OF PARALLEL PLATES.[1]

BY L. E. DODD.

EXPERIMENTAL work by the author in which simultaneous optical and electrical measurements were made of the distance between conducting flats in air required the application of a formula for distance in terms of electrical capacity. While the particular formula for the case of a limited area in extensive parallel plates was employed, the apparatus used prevented parallelism of the flats, and the question arose as to the amount of error due to application of the formula for parallel plates. The application of this formula neglects edge corrections. An expression has been derived for a limited area in extensive non-parallel plates which in its application to the apparatus must also neglect edge corrections. If edge corrections are neglected the lines of force may be considered arcs of circles, which is consistent with a result derived by others from a special transformation with conjugate functions.[2] The present derived expression for electrical capacity of non-parallel plates is,

$$C = W/4\pi \cdot \log (r_2/r_1) \cdot 1/\theta,$$

where W is width of plates (supposed of like dimensions and symmetrically situated), r_1 and r_2 the distances to the vertex from lower and upper edges (parallel to vertex) respectively of a plate, and θ is the angle between the plates. This formula is seen to be of a form similar to that for parallel plates, *i. s.*, a constant multiplied into the reciprocal of a distance. Further comparison of the two formulas reveals that the error in applying the latter for the former (neglecting error due to edge corrections) depends alone on the ratio (r_2/r_1), and is negligible over the range of values, 1 to 1.5, particularly in the author's experimental work,[3] and also in work of F. C. Brown,[4] and in unpublished work of G W. Stewart.

* STATE UNIVERSITY OF IOWA,
IOWA CITY, IA.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

[2] See Jeans, Elec. and Mag., 2nd ed., sec. 318, p. 268.

[3] Dodd, PHYS. REV., Vol. V., No. 1, Jan., 1915, p. 78.

[4] Brown, PHYS. REV., Vol. II., No. 4, Oct., 1913, p. 314.